FINAL REPORT

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Project Title: Preventing Strength Loss of Unbleached Kraft Pulp

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2. International Paper, a major producer of paper and paperboard, in-kind support equal to at least 10% of the total project value. Support consists of staff time that benefits the goal of the project. Contacts: Zheng Tan, (513) 248-6095, Zheng.Tan@ipaper.com; Xuan Nguyen, (513) 248-6073, xuan.nguyen@ipaper.com.

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EXECUTIVE SUMMARY

How the Research Adds to Our Understanding

Kraft pulp fibers lose inter-fiber bonding ability when they are dried during the manufacture of paper. Adverse environmental consequences of this loss include (a) limitations on the number of times that kraft fibers can be recycled, (b) reduced paper strength, sometimes making it necessary to use heavier paper or paperboard to meet product strength requirements, increasing the usage of raw materials, (c) decreased rates of paper production in cases where the fiber furnish has been over-refined in an attempt to regain inter-fiber bonding ability. The present study is the first of its type to focus on unbleached kraft fibers, which are a main ingredient of linerboard for corrugated containers. About 90 million tons of unbleached kraft fiber are used worldwide every year for this purpose.

Our DOE-funded research demonstrated the feasibility of two contrasting strategies to deal with strength loss due to drying of unbleached kraft fibers. First, our work showed that it is mechanistically possible to “prevent” or “block” the processes responsible for loss of bonding ability when the fibers are dried. It was found that the loss of bonding ability was associated with effectively irreversible closure of porosity within the cell walls of the fibers; it was possible to partly block such loss of porosity by drying the fibers in the presence of concentrated sugar solutions. Our work also showed the feasibility of a more realistic strategy - to minimize loss of bonding ability by avoiding conditions of over-drying. Surprisingly, conditions of pH and refining history did not appear to play significant roles relative to strength loss or pore closure, within the ranges typically encountered in containerboard production.

Second, it was found that certain polymeric additives, when added to never-dried, refined kraft fibers, produced strength benefits for both the initial paper and recycled paper produced from the same fibers with no further chemical treatment. In fact, the relative impact usually was greater in the case of the recycled test sheets, even though the chemical treatment had been limited to addition of strength agent to the never-dried, refined fibers. Particularly promising results were achieved under conditions in which the fiber surfaces were treated with a saturated layer of positively charged polyelectrolyte, followed by a negatively charged dry-strength additive. It was shown, in principle, that the optimum dosage of chemicals can be controlled by means of charge analysis tests. The mechanism of action of such chemical additives appears to be independent of the mechanism responsible for the observed strength loss when fibers are dried.

Recent work, since the previous annual report, probed the relationships between fiber bonding, fiber flexibility, paper density, and post-refining of kraft fibers. It was found that the flexibility of wet fibers is highly correlated with the resulting paper strength; however, flexible fibers tend to lose their flexibility upon drying. Tests were conducted in which the apparent density of paper was varied by changing the wet-press load. Results confirmed our earlier conclusion that the observed strength losses cannot be overcome by simply increasing wet pressing (as in the installation of a shoe press on an existing paper machine). Additional refining appears to be one of the most promising ways to restore bonding ability to kraft fibers, though one must keep in mind that each application of refining tends to make the resulting paper web harder to dewater, often requiring a slower rate of production.

Technical Effectiveness and Economic Feasibility

Certain of the project findings can be implemented immediately in paper mills, as mill operators work towards implementation of "best practices." Elements of these "best practices" are being communicated to potential users of the technology by means of a series of research articles (see list, with abstracts, near to the end of this report). Based on the research findings it is recommended to focus implementation efforts in two areas - *prevention* and *active treatment*.

With respect to preventative measures, the present results can be acted upon whenever paper machine equipment is either upgraded or replaced, making it possible to more accurately control the moisture content of paper. Many papermakers are not sufficiently aware of the harmful effects of over-drying. There is a common practice of temporarily drying paper products to moisture contents in the range of 1-5%, which is below the equilibrium moisture content at which the paper is delivered to customers and used. A primary reason for such drying strategies has been to overcome effects of moisture streaks. Over-drying of paper, even if the moisture is added back at a calender stack (paper passing through nips between smooth rolls) of a paper machine, is very energy-intensive, raising the cost of production. It can be expected that the double incentive of energy savings and reduced fiber damage will help to motivate papermakers to upgrade their equipment and otherwise adopt strategies that keep the paper moisture content at or above the target level at all times.

The impact of more uniform drying and the avoidance of excessively low moisture conditions can be expected to contribute a just few percentage points of improved paper strength – but those gains will be spread over many tons of product. Realistically there is probably potential to significantly upgrade at least 20% of existing linerboard paper machines in the next decade or two, representing about 18 million tons per year. Based on a nominal price of $500 per ton, if one assumes that strength differences can account for a 2% change in the amount of raw material required, these values imply a worldwide impact of $180 million per year.

With respect to active treatment strategies, the present results show that there are opportunities for more effective use of dry-strength chemicals, and that the effects of such chemicals can be very important when the fibers are recycled into new products. To achieve these gains it is necessary for papermakers to increase their adoption of monitoring and control equipment for paper machine wet-end chemistry. Further work needs to be done by chemical companies in order to identify the additives and treatment conditions that make best economic sense for a give paper grade and furnish. The present results can provide guidance for optimization of the treatment conditions, so that the chemicals used in one cycle of papermaking are still available at the fiber surfaces to contribute bonding ability when the fibers are recycled.

Benefits to the Public

Society benefits each time that the paper industry is able to implement the next generation of technology to save or re-use fiber resources. The bonding strength of fibers is critical, since product weight tends to be an inverse function of strength. Anything that we do to make the paper inherently stronger means that less material will be required. In addition to saving natural resources, less energy will need to be expended in transportation of the paper itself – even in cases where its main role is to aid in the efficient, breakage-free transportation of

something else contained within the paper box or bag. Society benefits further each time that the paper industry finds ways to recycle more of the fibers, keeping the harvesting of wood below the replacement rate of new trees that are grown for the purpose of paper manufacture.

Incentive plan: Although some recommendations of the present research project are likely to be adopted by various paper companies as a matter of self-interest, it also is worth seriously considering the relative costs and benefits of having a nationwide or worldwide incentive plan. Such an incentive plan could, for instance, involve a certificate to be placed on those products that are made under conditions that minimize damage to the fiber resources in terms of their ability to be recycled. As in the case of the ISO certification programs, the certificate would likely require documentation that each manufacturing facility has an active program to avoid conditions of over-drying. Though not considered in the present research project, it is reasonable to expect a certification of recyclability also to include consideration of avoiding excessive use of wet-strength agents, wax, sticky materials, and possibly certain kinds of inks. In the context of the present study, such an incentive plan would help balance the differing motivations of a producer of paper with the needs of users of the waste fibers. Presently there is not much incentive for the original papermaker to care about the quality of the fibers after they are recycled. Incentives can make it advantageous to use fibers that have been dried only to their target dryness, not beyond, and to which has been added either cationic or dual-polymer strength additives.

Background: Motivation for Project

Recycle of old corrugated containers (OCC) is a major success story for reduced net energy usage and landfill requirements. However, a strength problem adversely affects the economics of OCC use. Essentially irreversible loss in bonding potential occurs somewhere during the initial refining, pressing, and drying of virgin kraft pulps. In other words, the fibers achieve lower strength when they are recycled. Efforts to regain lost bonding potential by refining cause disproportionate freeness losses and higher fines levels relative to virgin kraft pulps. Past work suggested that most of the damage occurs as a result of drying.

The goal of the present study has been to evaluate potential low-cost strategies to treat the never-dried fibers in such a way as to block or otherwise compensate for the chemical mechanisms responsible for strength loss. Successful candidate treatment strategies should be simple, involve non-toxic materials, and require no significant new capital equipment or new unit operations. Treatments to be evaluated included products of guar, starch, acrylamide, urethane, surfactants, dye-analogues, and enzymes. Variables included molecular mass, the presence of hydrophobic groups, and the density of acidic groups. In response to input from the AF&PA panel, this research emphasized effects of process conditions in order to minimize the costs of chemicals and capital.

The initial phase of the project involved screening different treatment options relative to the initial strength of virgin handsheets and screening of the net effects on paper strength after the fibers are recycled. The first go-no-go decision point required that the project must identify promising strategies that do not adversely affect the strength of the virgin paperboard. The second go-no-go decision required that the project identify treatments of the never-dried pulp that achieve a net improvement in the properties of recycled paper. The third go-no-go decision

point required that the project identify one or more strategies that achieve at least a 25% improvement in strength, relative to the control case in which the never-dried pulp is not treated.

Successful project results will benefit integrated paper mills by increasing the strength contribution of broke, thus increasing product strength and reducing variability when broke levels change. Societal benefits will include increased recycling rates, lower net energy use, and lower chemical dosages or basis weight needed to achieve product strength specifications.

ACCOMPLISHMENTS vs. PROJECT GOALS

Project goals were spelled out in a series of milestone statements when the project was initiated in February of 2000. Each milestone was achieved, through to the formal end of the project in February 2003. The project was not selected for funding in the originally projected fourth year.

In addition to the original goals, supplemental funding from the National Science Foundation made it possible to extend the work in directions not foreseen in the initial project proposal. The following table shows the original milestones and their dates of completion.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
A	Strength of virgin board (End of Q4)	02/27/01	12/31/00	
B	Strength of recycled board (End of Q8)	02/27/02	12/31/02	
C	Closer simulation of mill (End of Q12)	02/27/03	12/31/02	
Task 1	Materials preparation (Q2)	06/30/00	06/30/00	
Task 2	Screening tests (Q4)	12/31/00	06/30/01	Extended through Q5
Task 3	Evaluation of treatments in lab recycling conditions (Q10)	06/30/02	06/30/02	
Task 4	Full simulation of wet-end chemistry in lab conditions (Q14)	06/30/03	Not funded	
Task 5	Pilot paper machine verification trials (Q16)	02/27/04	Not funded	
Task 6	Program management (Q16)	02/27/04	Not funded	

Some highlights of the completed work, including achievements not specifically included in the milestones, are listed below:

Project Highlights:

1. Eight articles for publication were completed, six of them to be published or already published in peer-review scientific journals. More details, including citation information and full abstracts are given in the final section of this report.

2. The first-ever screening study was completed of the effects of contrasting chemical treatments of unbleached kraft fibers relative to the strength of both the virgin paper and recycled paper made from the same fibers without further treatment. More details are provided in the Summary of Project Activities, which follows. Results are reported in the following article: Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Can Recycled Kraft Fibers Benefit from Chemical Addition Before They Are First Dried?," *APPITA J. 55* (3): 135 (2002).

3. Our work showed that at least two different mechanisms govern the adverse effects on kraft fibers when they are either dried (with or without heating) *versus* when they are heated without allowing them to dry. Results related to bleached kraft fibers will appear in the following article: Welf, E., Venditti, R. A., and Hubbe, M. A., "The Effect of Heating and Drying on the Properties of Recycled Papermaking Fibers," in preparation. Results related to unbleached kraft fibers are presented in the following publication: Hubbe, M. A., Venditti, R. A., Barbour, R. L., and Zhang, M., "Changes to Unbleached Kraft Fibers Due to Drying and Recycling," *Progress in Paper Recycling 12* (5): 00 (2003), in print.

4. Support was found for a hypothesis that the observed strength loss due to drying of unbleached kraft pulp is related to closure of micro-pores in the cell walls of fibers, and that at least some of these pores fail to reopen when the fibers are placed back into water solution. Results are shown in the following article: Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "The Prevention of Strength Loss of Recycled Paper by the Addition of Sugar during the Initial Drying or Virgin Unbleached Kraft Pulp Fibers," *J. Pulp Paper Sci.*, submitted.

5. New evidence was found that water-soluble polymers can add to the strength of both virgin paper, and also of recycled paper made from the same fibers without further chemical or significant mechanical treatment. It was shown that the results of dual-polymer treatment could be maximized under conditions corresponding to "saturation" of the fiber surface with material having a positive electrical charge. In principle one can use electrokinetic test results to optimize and control polymer dosages to achieve the maximum effects with a minimum of environmental impact. Results are given in the following paper: Hubbe, M. A., Jackson, T. L., and Zhang, M., "Fiber Surface Saturation as a Strategy to Optimize Dual-Polymer Dry Strength Treatment," *TAPPI J*,. submitted.

6. Recent results showed a connection between fiber flexibility, fiber water-holding ability, and inter-fiber bonding ability. Though flexibility of never-dried fibers was found to be dependent on the pH of the suspending medium, this difference disappeared when the fibers were dried. It appears that the more flexible, more bondable fibers under higher pH conditions are also more prone to loss of flexibility when they are dried. Results will be reported in the following articles: Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "The Prevention of Strength Loss of Recycled Paper by the Addition of Sugar during the Initial Drying or Virgin Unbleached Kraft Pulp Fibers," *J. Pulp Paper Sci.*, submitted; and Hubbe, M. A., Venditti, R. A., Barbour, R. L., and Zhang, M., "Changes to Unbleached Kraft Fibers Due to Drying and Recycling," *Progress in Paper Recycling 12* (5): 00 (2003), in print.

7. New evidence was found that both fiber flexibility and inter-fiber bonding – but not water retention – could be restored to a significant degree by mechanical refining of once-dried unbleached kraft fibers. It is worth noting that these most recent experiments, showing some conditions where refining obscured the effects of drying history of the fibers, also confirmed the earlier findings about the harmful effects of drying in the absence of any refining. Further work will be needed in order to define refining conditions that can achieve meaningful benefits with a minimum harm to such parameters as fiber length, fines content, and pulp freeness (ease of dewatering). Results are presented in the following article: Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Effect of Refining on Changes to Sugar-Treated Kraft Fibers during Recycling," in preparation.

8. Early in the project it was concluded, based on results of screening tests, that there was only a weak relationship, if any, between the apparent density of the paper test sheets and their physical strength properties. An attempt to "normalize" the screening test results to the same density, based on an assumed linear relationship between density and strength, did not change any of the initial conclusions regarding recycling effects and chemical pretreatments. Rather, the procedure merely amplified random errors in the data. Further experiments were undertaken, still relatively early in the project, to prepare paper handsheets under different conditions of wet-pressing; these early experiments were inconclusive, possibly because of the pressing conditions that were chosen. Recently the experiment was repeated again, focusing on the baseline condition of no chemical treatment. Pressing conditions were selected to allow an unambiguous interpolation to compare the strength properties of virgin and once-dried, recycled paper sheets at pre-selected values of apparent density. Results, which are spelled out later in this report (see Summary of Project Activities), showed that the observed effects of drying on recycled paper strength *cannot* be overcome by merely changing the conditions of wet-pressing (as in the installation of an extended-nip press).

SUMMARY OF PROJECT ACTIVITIES

Because all of the project results prior to March 2002 already appeared in the previous annual project report (April 2002), the present report will start with a summary of the most recent findings. These recent findings will then be followed by a chronological account of project activities, starting at the beginning of the project.

Recent Findings Concerning Apparent Density

Past studies often show a strong, essentially linear relationship between paper strength and apparent density (see, for instance, Guest and Weston in *Recycling Paper,* TAPPI, 1990, vol. 1, p. 169). Based on such studies it would appear that by varying the applied load or dwell time in a wet-press nip it should be possible, in principle, to achieve a wide range of strength targets, regardless of the quality of the fibers. In particular, it would appear reasonable to increase the press loading when making paper from recycled kraft fibers, since such fibers are tend to produce weaker, but less dense paper.

The effect of recycling on paper density was confirmed during the initial screening phase of the present work. In those tests the conditions or sheet-forming and wet-pressing were kept constant, and the apparent density was treated as one of the dependent variables. Typical results were reported as follows (see more detail in the Chronological Summary section later in this report):

Type of Paper	Apparent Density (cm^3/g)	Breaking Length (km)
Virgin handsheets	0.71	5.6 ± 0.6
Recycled handsheets	0.66	3.8 ± 0.4

It is worth noting, in the table above, that the tensile strength (indicated by the length of paper that just can support its own weight) was lower in the case of the unbleached kraft handsheets formed after the same fibers were recycled without further mechanical treatment. It is reasonable to ask, when considering the results shown above, whether it would be possible to achieve an equivalent tensile strength if the recycled handsheets had been processed in such a way as to match the apparent density of the virgin handsheets. To answer this question, our approach was to make primary handsheets and recycled handsheets, both at two different levels of pressing. The fiber was unbleached kraft pine pulp, refined at 9000 revolutions with a PFI mill.

Refined fibers were dispersed in a TAPPI disintegrator for 5 minutes before making handsheets, following TAPPI Method T205 except that the basis weight was approximately double in the standard amount and the pressing pressure was adjusted to “low” and “medium” levels of 10 psi and 30 psi respectively. The handsheets were dried in a TAPPI condition room for 48 hours before physical testing. To make recycled paper, primary handsheets made at 30 psi wet pressing pressure were soaked in tap water for 6 hours before being dispersed in a TAPPI disintegrator for 5 minutes. The dispersed fiber slurry was to form recycled handsheets following the TAPPI procedure except the pressing pressure with 30 psi and 60 psi respectively. The handsheets were dried in a TAPPI conditioned room for 48 hours before physical testing.

Results are shown in Figs. 1 and 2. Limit bars indicate 95% confidence intervals for the mean values of the test results.

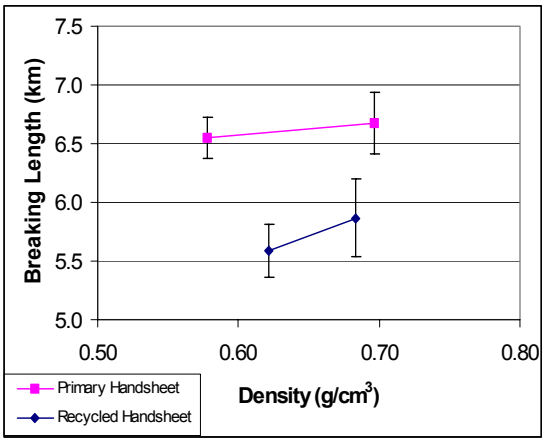

Fig. 1 Effect of density on breaking length

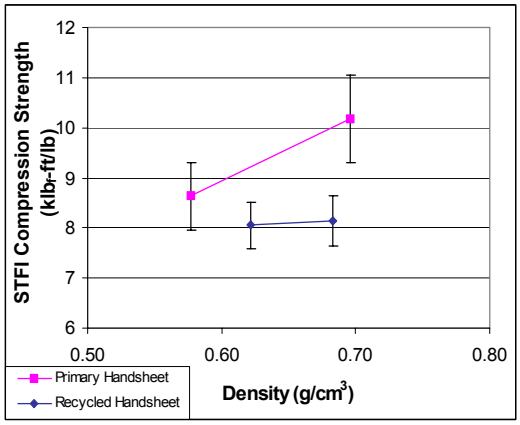

Fig. 2. Effect of density on STFI compression strength

As shown in Figs. 1 and 2, increasing wet pressing pressure during making recycled handsheets could not recover the loss of paper strength significantly. At the same level of apparent density, recycled handsheets had lower strength compared to primary handsheets. That meant that the effect of drying on paper strength could not be removed by merely wet pressing more during making recycled handsheets, if one compares them under an equal apparent density.

Fiber Flexibility

Some test results related to fiber flexibility were reported in the previous annual report, but related work continued into the final year of the project. The pH range of the investigation was extended up to pH=10. In order to determine the effect of soaking time on fiber flexibility, a standing time of 24 hours was used before flexibility testing for never-dried, unrefined fibers Four different pH conditions (pH=3, pH=4.5, pH=6 and pH=8) were carried out to find the effect of pH on the fiber flexibility of the oven-dried fibers. The pH and conductivity changes of the fiber solutions with standing time were observed.

Tests conditions included never-dried original unrefined, unbleached softwood pulp (same as used previously), with the pH adjusted with either 4N sulfuric acid (H_2SO_4) or 0.25N sodium hydroxide (NaOH). Observations were made with an Olympus BH2-UMA microscope, based on the procedure of Steadman and Luner ("The Effect of Wet Fiber Flexibility on Sheet Apparent Density," *Papermaking Raw Materials Transactions of the Eighth Fundamental Research Symposium*, edited by Punton, V., Mechanical Engineering Publications limits, London, Vol. 1, pp. 311-337, Sept. 1985). Because of an unexpected accident, the compression air was unavailable when we were making slides for fibers equilibrated at pH=6 and pH=8. These slides had to be delayed another 24 hours before measuring the fiber flexibility. That means the standing time for these pH conditions were 48 hours. The oven-dried

fibers (12 hours at 105°C) were soaked with 1000 ml deionized water for 12 hours in a beaker before dispersed in disintegrator for 5 minutes. After that, the fiber solution was washed thoroughly in a large excess of deionized water followed by adjustment the slurry to a certain pH value (pH3, pH4.5, pH6 and pH8) by 4N sulfuric acid or 0.25N sodium hydroxide and allowed to stand in water 24 hours (for fibers of pH6 and pH8, the time was 48 hours in this study) before measuring fiber flexibility. Around 5 ml of this slurry (1% concentration) was used to make slides for each fiber flexibility test. The pH value and conductivity of pulp solutions were measured before also after the adjustment.

Baseline tests: Because each test of fiber flexibility involved measurements of many fibers, and because of such factors as seasonal variations (*e.g.* springwood *vs.* summerwood fibers) it makes sense to compare the results in terms of distributions. Except for monthly reports to the industrial co-sponsors, these distribution plots have not been submitted for publication. As shown in Figs. 3 and 4, drying of the unbleached kraft fibers at an unadjusted pH of approximately 6 yielded a noticeable shift in the distribution of fiber flexibility:

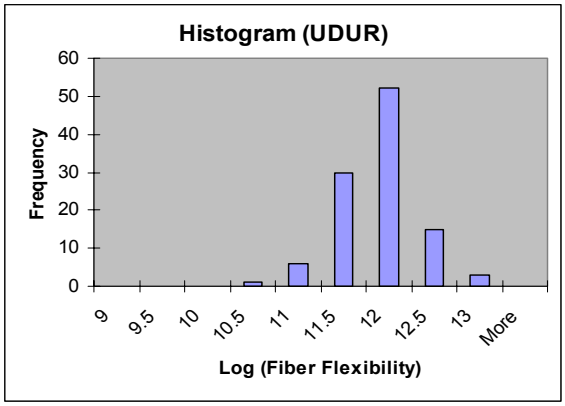

Figure 3. Distribution of flexibilities in a sample of never-dried UBK fibers.

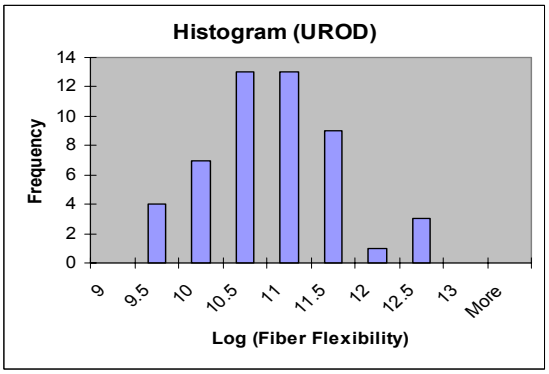

Figure 4. Distribution of flexibilities in a sample of oven-dried (105 ^{o}C, 12 hr) fibers.

Soaking period: Before proceding further with the analysis, there was a concern that possibly some of the observed effects might have been due to differences in the soaking periods, prior to flexibility testing, that had been experienced by different batches of fibers. As shown in Table 1, increased soaking time yielded only a small increase in fiber flexibility, relative to the size of the changes caused by pH differences and other factors to be discussed.

Table 1. The Effect of Standing time on Fiber Flexibility

Samples	Average	Median	3rd Quartile
UDUR pulp (0 hr)	5.38E+11	3.51E+11	6.64E+11
UDUR pulp (24hrs)	6.72E+11	4.26E+11	7.21E+11
UD: Never Dried; **UR**: Unrefined			

Figures 5 and 6 show the results from Table 1 in terms of a distribution. Note the high degree of similarity of the results, independent of soaking time. The main difference between the two plots can be seen in the left-hand "tails" of the distributions. Apparently, soaking mainly increases the flexibility of a few of the fibers that were among the stiffest, when first tested.

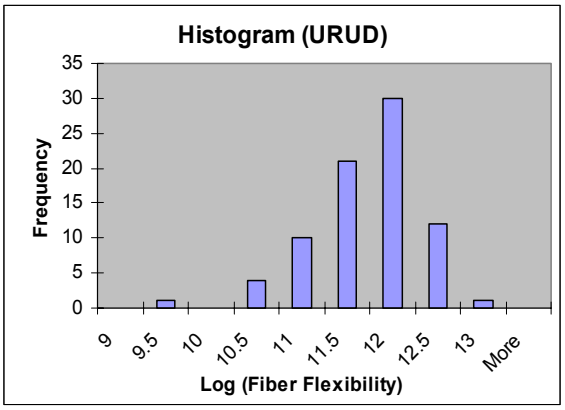

Figure 5. Test immediately after washing by deionized water.

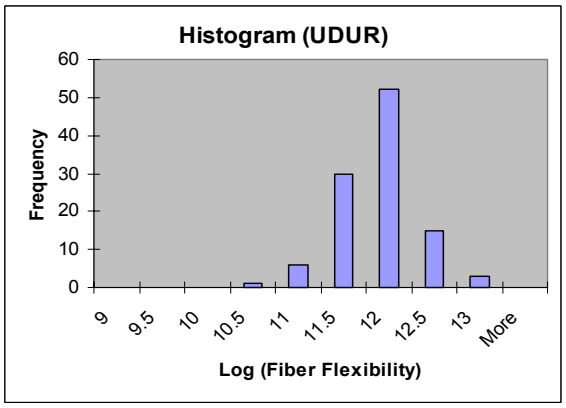

Figure 6. Stand in deionized water for 24 hrs before test.

Effect of pH, never-dried: Table 2 shows the effect of pH on flexibility of never-dried, unrefined UBK fibers as a fuction of the pH of the solution. There was a trend towards increasing flexibility with increasing pH. Though this trend is consistent with an expected increase in fiber swelling with increased pH, the effect shown here has not previously been demonstrated. Lindström and Kolman (*Svensk Papperstidn. 85*: R143, 1982) showed related results in which the tensile strength of paper made from never-dried fibers increased with increasing pH prior to paper formation.

Table 2. The Effect of pH on Fiber Flexibility of Never Dried Fibers

Sample	Average	Median	3rd Quartile
UDUR @pH 3.0	5.91E+11	3.32E+11	8.61E+11
UDUR @pH 4.5	8.21E+11	4.98E+11	8.35E+11
UDUR @pH 6.0	1.15E+12	6.82E+11	1.30E+12
UDUR @pH 8.0	1.11E+12	6.84E+11	1.31E+12
UDUR @pH 10	1.06E+12	7.09E+11	1.26E+12
UD: Never Dried; **UR**: Unrefined			

Figures 7 through 11 show the same information, except that distributions of fiber flexibility are plotted, rather than averages. Again, one can see that the distributions tend to move towards higher values of fiber flexibility with increasing pH.

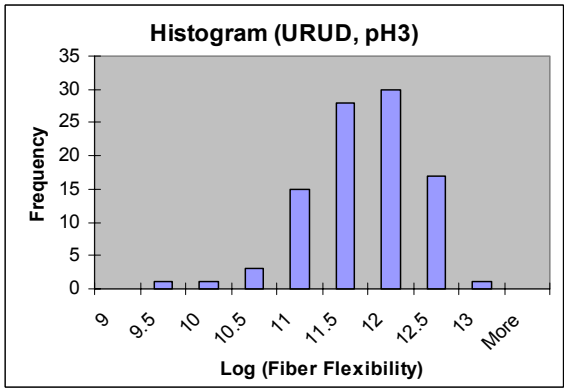

Figure 7. Stand in deionized water for 12 hrs after pH adjustment.

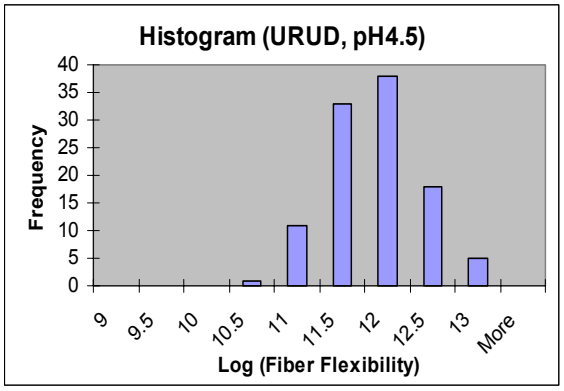

Figure 8. Stand in deionized water for 12 hrs after pH adjustment.

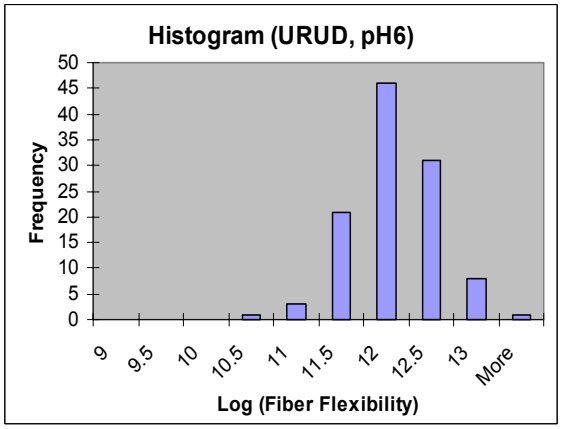

Figure 9. Stand in deionized water for 12 hrs after pH adjustment.

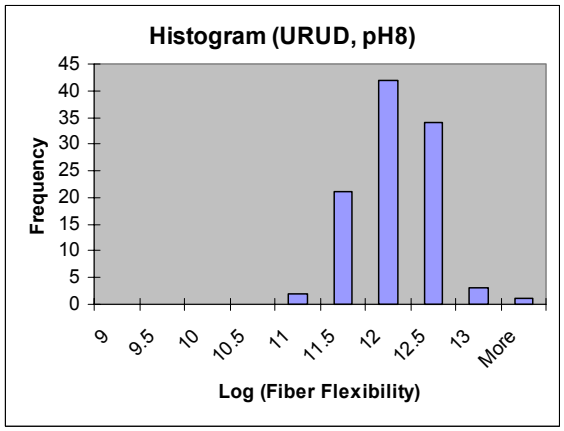

Figure 10. Stand in deionized water for 12 hrs after pH adjustment.

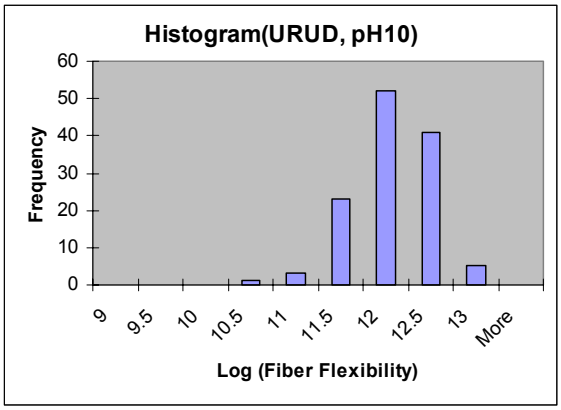

Figure 11. Stand in deionized water for 12 hrs after pH adjustment.

Effect of initial pH, after drying and redispersion: Oven drying was carried out in this series of tests at 105 ^{o}C for 12 hours. Though the temperature of these tests can be considered as realistic, the drying time represents an extreme of over-drying. For all initial pH values, the dried fibers were redispersed in near-neutral tap water. Results in Table 3 show no significant effect or trend. This lack of a trend may be considered surprising in light of what already has been shown in the case of never-dried fibers. However, it is worth reconsidering a mechanism proposed by Pycraft and Howarth (*Paper Technol. Ind. 21*, 12: 321, 1980). These authors said, in effect, that factors leading to better bonding the first time around can make the fibers more susceptible to loss of bonding ability after they are recycled. Indeed, it is reasonable to expect more flexible fibers to experience a greater degree of closure of pores in the cell walls.

Table 3. The Effect of PH on Fiber Flexibility of Oven -Dried Fibers			
Samples	**Average**	**Median**	**3rd Quartile**
ODUR @pH3	2.66E+11	8.56E+10	2.71E+11
ODUR @pH4.5	1.69E+11	6.52E+10	1.84E+11
ODUR @pH6	1.78E+11	1.15E+11	2.51E+11
ODUR @pH8	2.89E+11	8.85E+10	2.00E+11
Note: **OD**: Oven Dried; **UR**: Unrefined			

The results from Table 3 are shown in Figs. 12 through 15, again showing the lack of a clear trend in flexibility with original pH, after oven-drying.

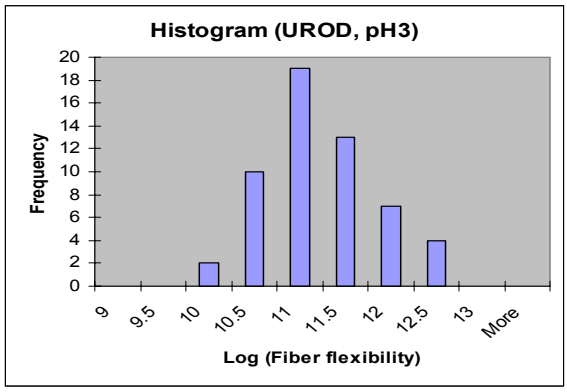

Figure 12. Stand in deionized water for 24 hrs after pH adjustment.

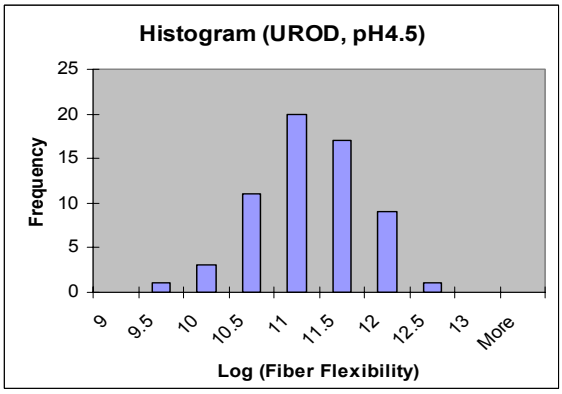

Figure 13. Stand in deionized water for 24 hrs after pH adjustment.

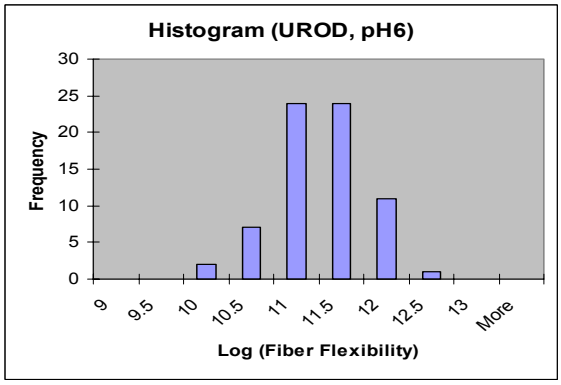

Figure 14. Stand in deionized water for 48 hrs after pH adjustment.

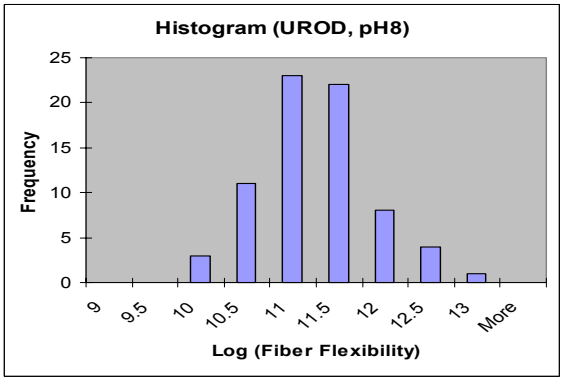

Figure 15. Stand in deionized water for 48 hrs after pH adjustment.

Effect of Wet-Pressing: Figure 16 shows that wet pressing and drying reduced the flexibility of fibers, and oven drying had the most significant effect on the reduction of fiber flexibility. This finding is consistent with the loss of paper strength and water retention values. It is known that drying temperature of primary handsheets is important to recycled handsheets that are made from their primary handsheets. Oven drying deteriorates the fiber more than air-drying does. The strength of recycled paper made from oven-dried fibers is lower than that of recycled paper made from air-dried fibers. Water retention values follow similar trends. The possible reason is that oven drying increases the degree of crystallization of fiber surfaces and fibers become stiffer. The increased stiffness can be expected to reduce the relative fiber bonded area. Figure 17 shows that the flexibility of unrefined fibers has same trend as that of refined fibers and refined fibers are more flexible than unrefined fibers. In this way, the results of flexibility tests

support the conclusions that handsheets made from refined fiber have higher relative bonded area and stronger paper strength.

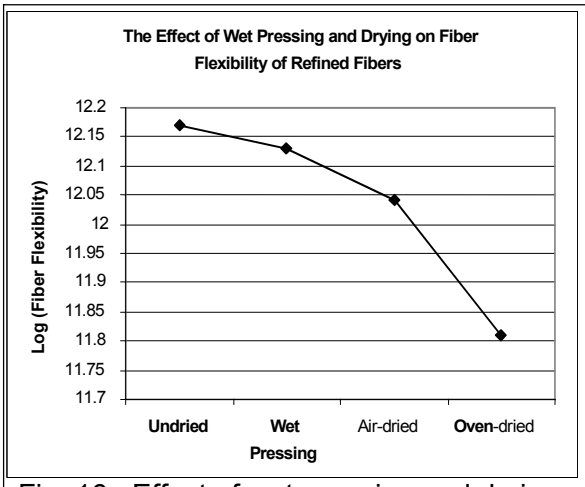

Fig. 16. Effect of wet-pressing and drying on fiber flexibility of refined UBK fibers

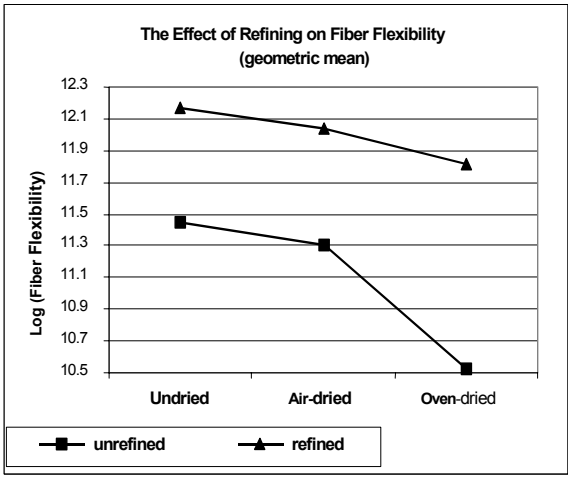

Fig. 17. Effect of refining on fiber flexibility (geometric mean)

Effect of Sugars on Fiber Flexibility: It was observed during the initial screening phase of the study that sugars have positive effect on paper strength, when comparing fibers that had been dried after exposure to aqueous environments. One hypothesis is that sugars can enter fiber pores and either prevent pore collapse or make it so that any such collapse is easily reversible when the fibers are rewetted. Reduced irreversible pore collapse can explain the fact that there was less hornification of the fibers, *i.e.* less reduction in WRV. Since the fiber flexibility test is a very useful approach to observe the change of fiber flexibility during drying, this kind of test may determine the effect of sugars on fiber flexibility.

The results in Fig. 18 show that refined fibers treated by sugars before drying were more flexible after drying and reslurrying than untreated refined fibers subjected to the same conditions. Fibers had higher flexibility after treatment with 10% sugar solutions, compared to those treated with 2% sugar solutions, again with the evaluation taking place after the dried fibers had been re-dispersed. It makes sense from the results because 10% sugar solution has more molecules than 2% sugar solution's. There should be more sugar molecules staying inside the fiber pores during drying. The more the chemical inside pores, the more pore closure is prevented. Physical test results indicated that handsheets made from sugar treated fiber were stronger than handsheets made from untreated fibers subjected to the same drying conditions.

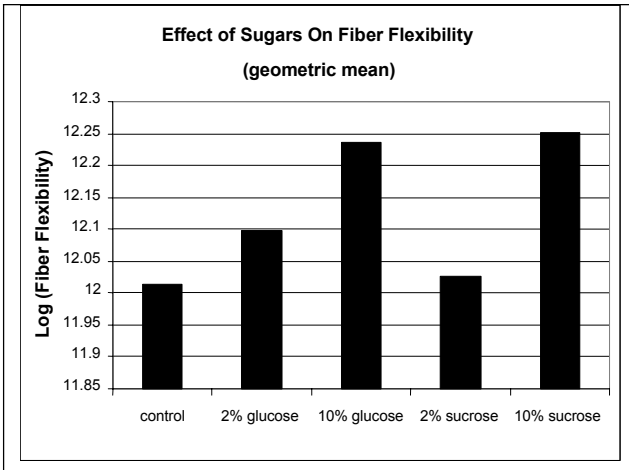

Figure 18. Effect of sugars on fiber flexibility

Since the structural composition of wood fibers is complicated, it is unreasonable to expect all fibers have same physical properties. For example, there is a distribution of fiber lengths in each sample. In order to more clearly understand the effects of treatments on fiber properties, the distribution of fiber flexibility will be helpful. Figures 19 and 20 show the distributions of flexibility of control experiments and fibers treated by 10% glucose solution, respectively. It is apparent from these results that treated fibers were more flexible than untreated fibers.

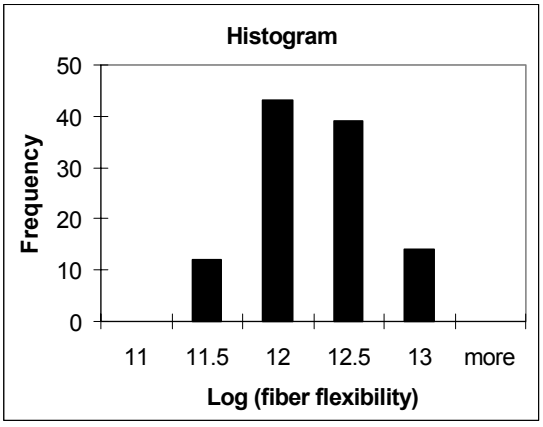

Fig. 19. Flexibility distribution of untreated fibers (fiber pad method)

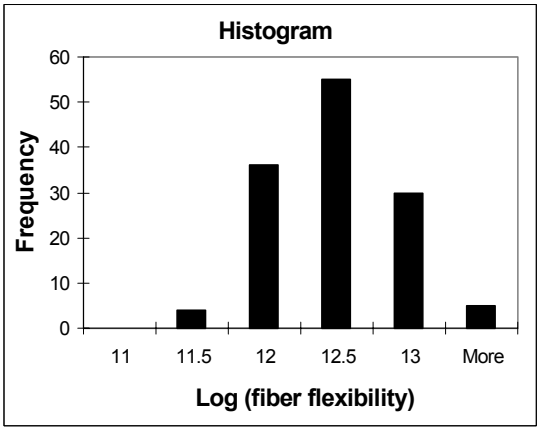

Fig. 20. Flexibility distribution of fibers treated by 10% glucose solution.

Effects of Aqueous Environment on Fiber Flexibility: It is known that the environment of papermaking has big effect on final paper strength. This implies that the environment affect the fiber properties. Since there is not information about fiber flexibility available from publications, further work was done in our laboratory. Water retention values of fibers decrease with increasing salt concentration. People have attributed this effect to the shielding effect of salt ions. The presence of the ions reduces the repulsion between the charged groups on the fiber surface. Figure 21 shows that the fiber flexibility was reduced with increasing salt concentration of pulp slurry.

Because relatively hard water is used in many paper mills and hardness is an important index for water quality, it is necessary to know the effect of hardness on the fiber. At the same time, it is well known that calcium ions form a complex with carboxyl groups. It is also known that calcium ion has more effect on water retention value that sodium ion. Therefore, it is interesting to know the effect of hardness on fiber flexibility. Fig. 22 shows that the fiber flexibility was reduced with increasing hardness of pulp slurry, consistent with this interpretation.

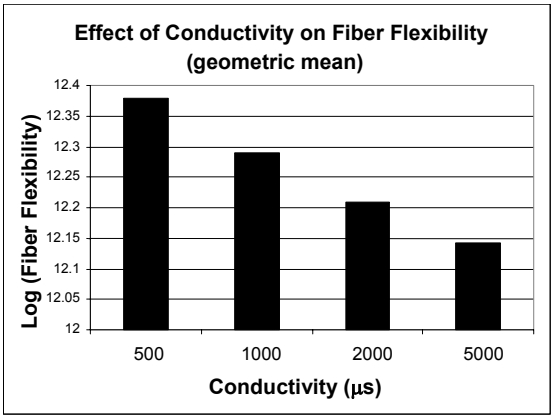

Fig. 21. Effect of conductivity on fiber flexibility (geometric mean)

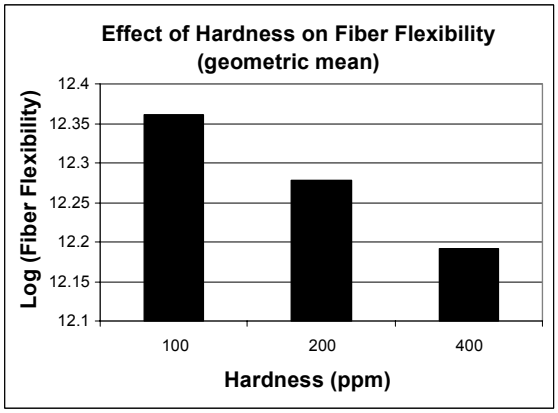

Fig. 22. Effect of hardness on fiber flexibility (geometric mean)

Effects of Sugars on Fiber Physical Properties

Since we found that sugars could prevent the strength loss of recycled paper and that the treated fibers had higher flexibility than untreated fibers, another experiment was set up to determine whether treatment by sugars had an impact on later refining, after the fibers were rewetted. The Fiber Quality Analyzer (FQA) was used in this study. Although the TAPPI disintegrator was designed with the idea of avoiding significant refining action, we were suspicious that the disintegrator may have a significant effect to shorten fibers, especially if fibers have become stiffer as a consequence of drying and recycling. As shown earlier, fiber length and fine content were measured by the FQA. Table 4 shows that the slurry of fibers that had been treated by sugar solutions before drying had less fines and slightly longer length

compared to the control experiment. This observation is consistent with the proposal that a less stiff fiber ought to be less susceptible to damage during refining.

Table 4. The Effect of Sugar on Refined Fiber Properties by FQA		
Samples	Percent fines	Fiber length
Control	26.93	1.32±0.07mm
2% sucrose solution	18.47	1.50±0.07mm
2% glucose solution	20.59	1.44±0.07mm
10% sucrose solution	18.40	1.51±0.07mm
10% glucose solution	21.80	1.37±0.06mm
Note: **1)** Fiber was defined as length greater than 0.07 mm in this table **2)** Column of Fiber Length shows a standard deviation		

Post-Refining

The addition of sugar to refined, never-dried softwood kraft fibers before drying showed that the sugar treatment improved the strength of recycled paper made from the corresponding re-slurried fibers, compared to the control test without sugar. Results from fiber flexibility tests showed that the sugar-treated fibers were more flexible, compared to untreated fiber. Tests of fiber length and fines content by image analysis (Fiber Quality Analyzer) also showed that untreated fibers tended to generate more fines and become shorter during dispersing in a TAPPI disintegrator after air-drying. Since, based on the previous literature, one should not expect a significant effect for a disintegrator to either reduce fiber length or create new fines during dispersing, we then examined the effect of severe drying (oven drying at 105 °C for 30 minutes) on fiber length and fines content during dispersing. However, if fiber pads made from sugar-treated fibers were oven dried and then refined before making recycled paper, no significant differences of paper strength were found in the recycled papers compared to the control experiment, and fiber length either, as well as fines content. Results from the fiber flexibility test showed that treated fibers still have higher flexibility compared to untreated fibers. The results indicated that mechanical force (refining) might have a dominant effect on fiber fibrillation and fines generation, and that the effects of refining can be obscure the influence of drying on the bonding properties and morphology of the fibers.

Experimental conditions were as follows for this series of tests: Reagent-grade sucrose (Fisher, Lot.701806) and anhydrous α–D-glucose (Aldrich, catalog number 158968) were used to determine the effect of sugars on the recycled refined-fiber properties including fiber length and fine content. Dextrose (D-glucose) anhydrous provided from Fisher (cat. No. D16-3) was used in the set of experiments for determining the effect of PFI refining on the sugar-treated fibers during recycling. All chemicals were used without further purification. Fiber characteristics were evaluated with a Fiber Quality Analyzer (FQA, OpTest Equipment Inc). Microscopic observations and digital images were obtained with an Olympus BH2-UMA microscope with Sony 3CCD Color Video Camera (Model: DXC-970MD). The images were captured and evaluated using Image-Pro Plus (Version 4.0, Media Cybermetrics) on a Windows 98 computer. Also micro glass slides (75mm x 50mm x 1mm, Fisher catalog number 125535B)

and stainless steel wire (25.4 μm, California Fine Wire Company) were used to prepare wired slides for fiber flexibility tests.

The procedure for this set of experiments is shown in Fig. 23. One control experiment involved measuring the effect of refining on the physical properties of the never-dried fibers. Another control experiment involved dispersing fiber pad, only without drying. The third control experiment was carried out in parallel with tests involving sugar treatment; such experiments involved fiber pad formation and air-drying. In this case, thirty grams of pulp were taken from cold storage and refined with a PFI mill (9000 revolutions). Two steps should be mentioned: one is that the sugar solutions were added to PFI refined pulp before making fiber pads; another is that the fiber pads were dried in a TAPPI condition room [50.0% ± 2.0% RH and 23.0 ± 1.0ºC] over 48 hrs.

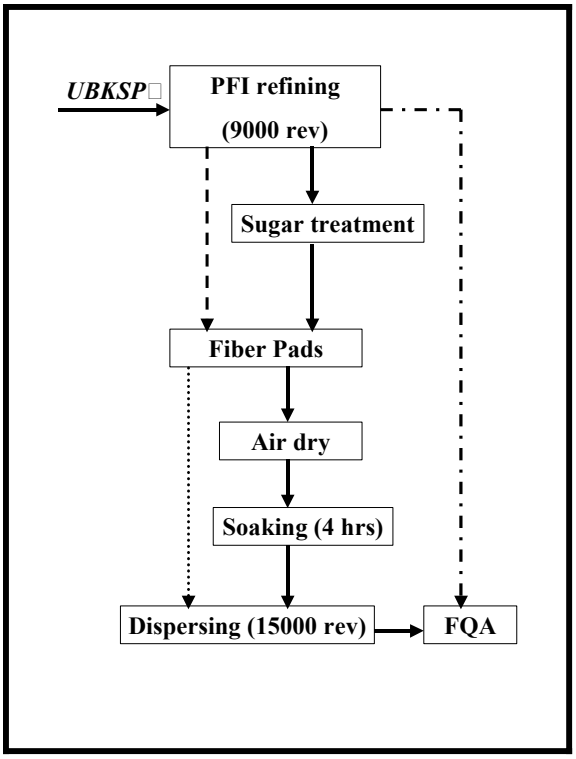

Figure 23. Experimental strategy for evaluating effects of post-refining of recycled UBK fibers.

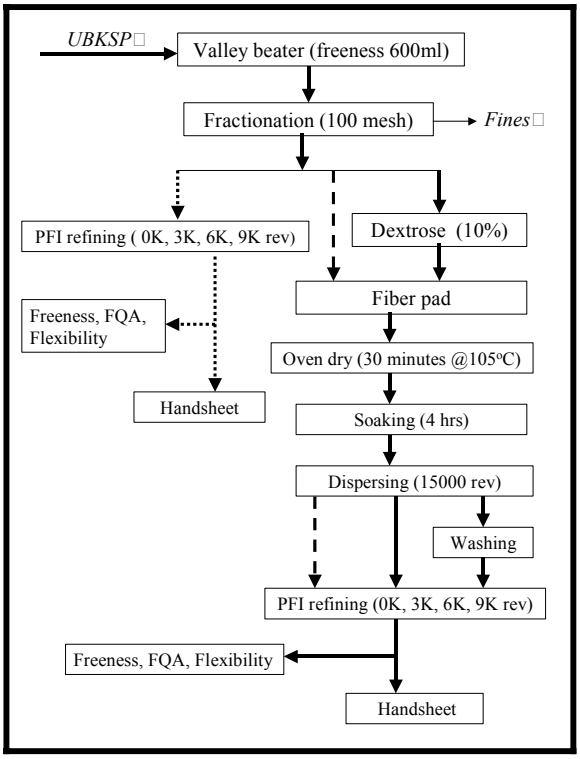

Figure 24. Procedure for the treatment with dextrose.

Effect of Dextrose: Results from the previous work showed that sugar-treated fibers were more flexible, compared to the control experiment, and also glucose had more effects not only on the flexibility of the recycled treated fibers, but also on the paper strength of the recycled paper made from the treated fibers. A question was raised: What would happen if dextrose (D-

glucose)-treated fiber pads were dried and then refined before making handsheets? Another set of experiments was conducted to determine whether treatment by dextrose had an impact on later refining, after the fibers were rewetted. Would the treatment increase recycled paper strength, or, if the treatment improved the fiber flexibility, did the increased flexibility from dextrose treatment result in less fines generation during refining of the recycled fibers?

As shown in Fig. 24, sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following the procedure of TAPPI method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 45 minutes to a freeness of approximately 600 ml. After that, fiber fines were removed via a 100-mesh screen by a Bauer-McNett classifier, following the procedure of TAPPI method T-233. In this procedure, dextrose solution was added to the fines-free slurry (*ca*. 0.6% consistency), and then extra water was added in order to reach a final concentration of dextrose of 10%. The mixture was stirred for 12 hours before making fiber pads on filter papers (Whatman #4). The fiber pads were dried in an oven for 30 minutes at 105 °C and then kept in a TAPPI condition room for 48 hours. The dried fiber pads were soaked for at least 4 hours and then refined by a PFI mill for a specified time (0, 3000, 6000, 9000 revolutions) following TAPPI method T248 before making handsheets.

Four features of the procedure steps need to be emphasized. First, in order to amplify the effect of sugar treatment, fibers were refined by the Valley beater at a relatively mild level. This was done because refining will tend to open up fiber pores and more sugar molecules will have a chance to enter and retain in the pores during drying. Second, in order to determine the exact amount of the fines generated during PFI refining, the primary fines were removed by 100-mesh screen of a Bauer-McNett classifier. Third, in order to maximize the effect of drying on fiber properties, thirty-minute oven drying at 105°C was adopted. Last, the effect of washing on the dextrose-treated and dried fibers before refining was also considered as shown in Fig. 24. In this case, the fiber slurry was washed by a large excess of deionized water. Before measuring fiber flexibility, the pulp slurry was washed thoroughly by excess deionized water and then kept in deionized water overnight.

Figures 25 and 26 show that the slurry of fibers that had been treated by sugar solutions before drying had fewer fines and slightly longer length compared to the control experiment. Results of replicate experiments are shown by the two symbols. The error bar in both figures shows a 95% confidence level. The observations were consistent with the proposal that a less stiff fiber ought to be less susceptible to damage during refining. As shown, there were no significant differences between the two sugar treatments, neither on fiber length nor on fines content.

Further explanation may be needed regarding the results of two control experiments not involving drying. On the other hand, why did fibers appear to be longer after being dispersed? One possible reason is that fiber was straightened during dispersing. Also, although the FQA is supposed to measure the actual fiber length according to the analyzer manual, still there is some doubt that the FQA analysis of fiber length is completely unaffected by curl.

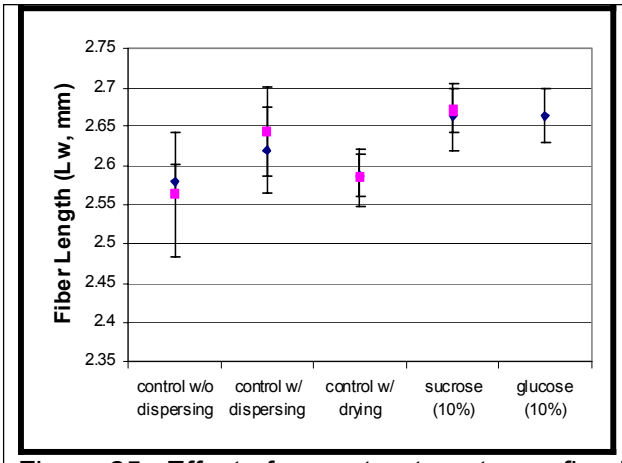

Figure 25. Effect of sugar treatment on refined fibers after recycling

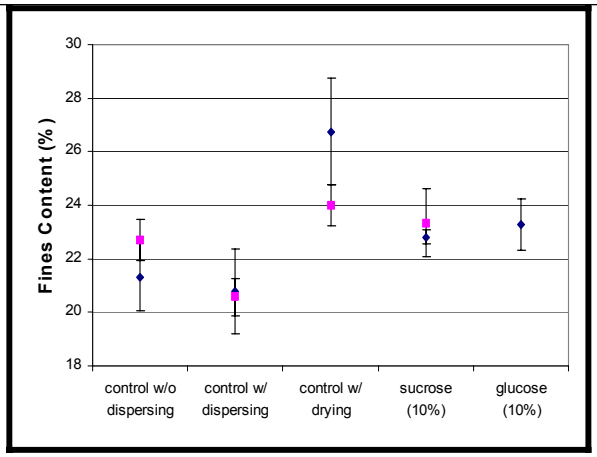

Figure 26. Effect of sugar treatment on refined fibers after recycling

Effect of PFI Refining on the Physical Properties of Dextrose-treated Fibers

It is well known that the freeness test is sensitive to the fines content of a fiber slurry. If a certain treatment reduces the generation of fiber fines during refining, then it is expected that the treated pulp should have a higher freeness value. In order to exclude the effect of the viscosity of sugar solution on the freeness test results, a preliminary experiment was conducted under different levels of glucose concentrations within the reasonable range. It was found that there was no difference in measured freeness among these different concentrations of glucose, as shown in Fig. 27. This result is important because the change of freeness value can be ascribed to the change of fines content only if one can exclude the possible effect of a change in solution viscosity. Although fiber fibrillation also affects the freeness, we did not expect that sugar would change the degree of fiber fibrillation if sugar added to a refined pulp before the freeness test.

Figure 28 shows that there was no significant difference among the treatments without any refining or a mild level of refining. However, results from Fig. 28 showed that there was a significant difference between the experiments involving drying without sugar and drying with sugar under a high level of refining. Could the difference be attributed to the difference in the generation of fines under different treatments? If this is true, under that refining condition, the freeness of the experiment involving drying without dextrose should be lower, compared to the experiment involving drying with dextrose. According to the previous work, untreated fibers were stiffer than sugar-treated fibers, and it was predicted that untreated fibers would generate more fines during refining. However, no significant difference was found for fines content, even after 9000 revolutions of refining as shown in Fig. 28. Using FQA to obtain fines content is not expected to be highly accurate. It is noted that our results were consistent with the work of Laivins and Scallan (in *Products of Papermaking,* Baker, C. F., Ed., Vol. 2, Pira, Leatherhead, UK), who used the traditional method to measure fines content. Laivins *et al.* found that drying-and-rewetting did not change the percentage of fines in either mechanical or chemical pulps, which disagrees with the findings of other researchers.

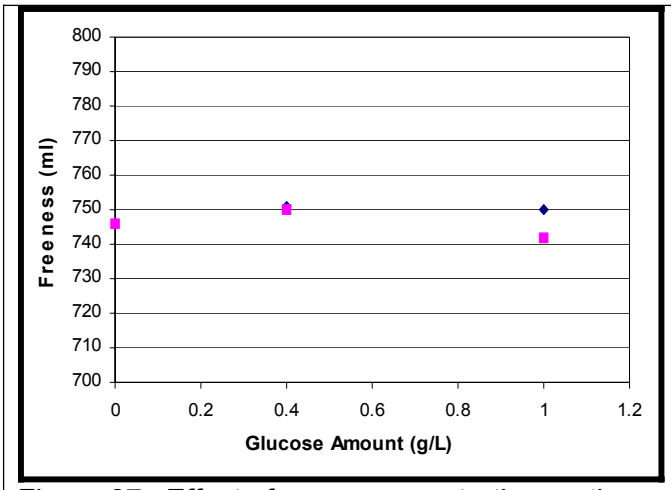

Figure 27. Effect of sugar concentration on the freeness test

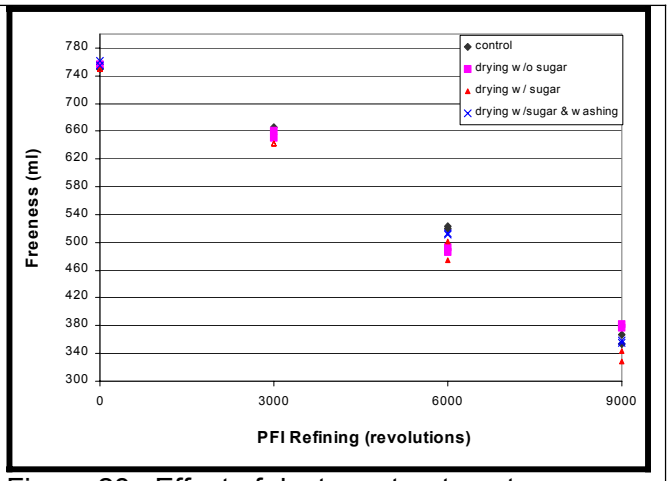

Figure 28. Effect of dextrose treatment on freeness during PFI refining

The results shown above indicate that there was another part of the story. As it is well known, the freeness of a fiber slurry is not determined by fines content alone; fibrillation of the fiber surface also is an important factor. The more fibrillation of a fiber surface, the more the water tends to be retained. In this case, treated fibers might tend to be more fibrillated during a high level of refining. Although the fine contents were the same for both conditions, it is hypothesized that fewer fines were generated and fewer fibers were cut during refining in the case of sugar-treated fibers. One possible reason is that the microfibrils were removed from fiber surfaces, and such detached fibrils can fall within the range of the definition of fines.

The fiber length under both situations may provide evidence to support this hypothesis. From Fig. 29 there was no significant difference for fiber length at 9000 revolutions refining between fibers treated by 10% dextrose solutions and untreated fibers involved drying at a 95% confidence level. A t-test showed that there was not any significant difference even at an 80% confidence level, but only at a 78% confidence level. Fig. 30 shows that without additional refining, there was a significant difference on fiber length between treated-fibers and untreated fibers, which was consistent with the results shown in Fig. 25.

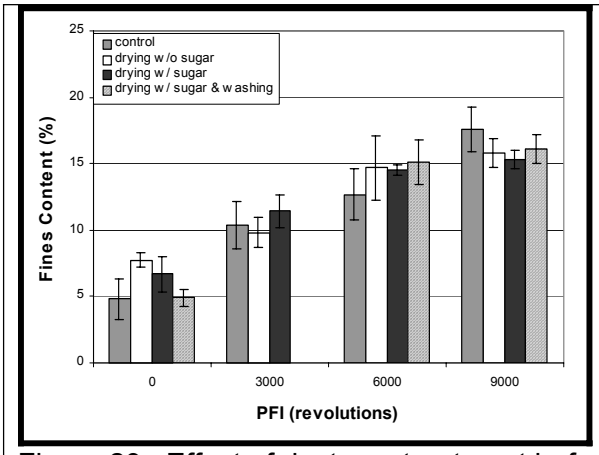

Figure 29. Effect of dextrose treatment before drying on fines generation during PFI refining

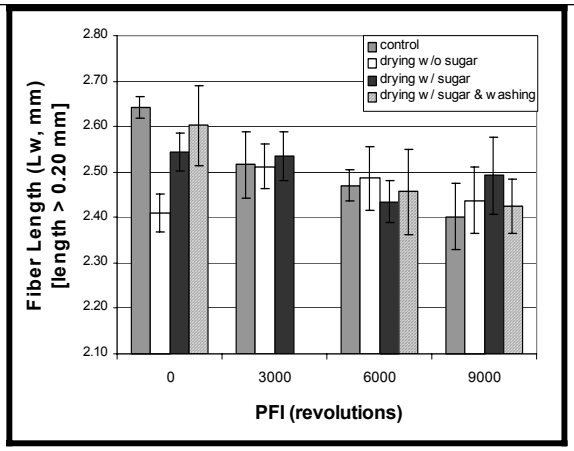

Figure 30. Effect of dextrose treatment before drying on fiber length during PFI refining

Figure 31 shows that the sugar-treated fibers maintained higher flexibility compared to untreated fibers when both were exposed to the same conditions of drying. The error bar shows a 95% confidence level. However, from Fig. 31, one cannot tell whether the difference on fiber flexibility is significant between fibers treated by dextrose and untreated fibers involved drying. A t-test showed that there is a significant difference on fiber flexibility between these two treatments at a 95% confidence level. Also a t-test showed that washing has a significant effect on fiber flexibility at a 90% confidence level. One possible reason is that removal of sugar from the fiber wall may facilitate fiber lamellas more easily slipping relative to each other during refining. So far there is not specific evidence to support such an explanation. Again it is noted that dried fiber has lower flexibility compare to a control experiment without involving drying.

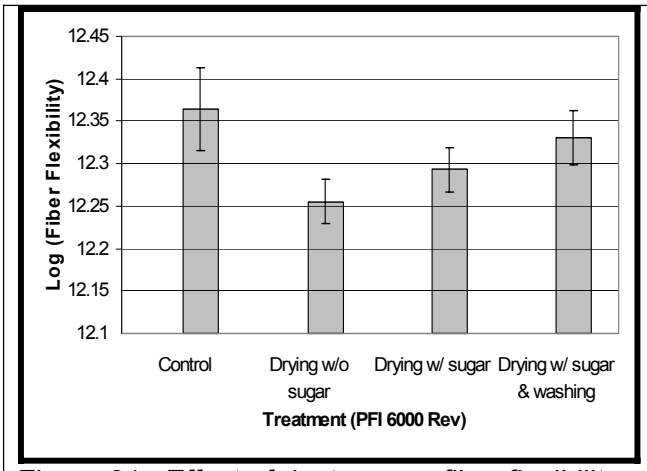

Figure 31. Effect of dextrose on fiber flexibility

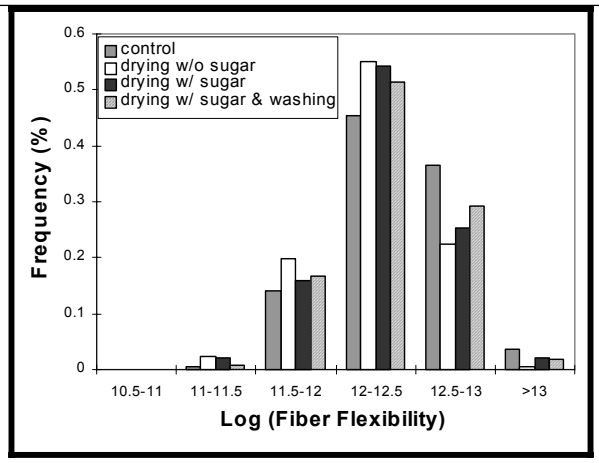

Figure 32. Effect of dextrose on fiber flexibility distribution

Figure 32 shows the distributions of fiber flexibility of this study. It can be observed for all samples that there is an approximately normal distribution of fiber flexibility when plotted on a logarithmic scale. It is clear that more treated fibers fall within the range of higher flexibility compared to the untreated fibers involving drying.

Effect of PFI Refining on the Recycled Paper Made from Dextrose-treated Fibers

We previously showed that paper made from recycled sugar-treated fibers without additional treatment had a higher paper strength (tensile strength and STFI compression strength), compared to paper made from recycled untreated fibers. A series of tests was carried out in which additional refining was applied before making recycled handsheets. In this context it was a surprise that drying did not have effect on paper strength of recycled handsheets made from recycled fibers involving a relatively high level of refining, as shown in Figs. 33 and 34. That means a certain refining can restore the paper strength. Many studies have shown that refining could restore the fiber swelling to the never-dried level. How can a fiber completely forget its "history" of drying-rewetting? Based on the work of Laivins and Scallan (in *Products of Papermaking,* Baker, C. F., Ed., Vol. 2, Pira, Leatherhead, UK), "the fines of a pulp are more swollen than the fibers by a factor of about 2 and the secondary fines of chemical pulps are much more swollen than the primary fines", also from our results of the fines content shown in Fig. 29, we may conclude that the total swelling of pulp slurry is independent of the treatments of this study. The freeness test shown in Fig. 28 also provided evidence to support this claim.

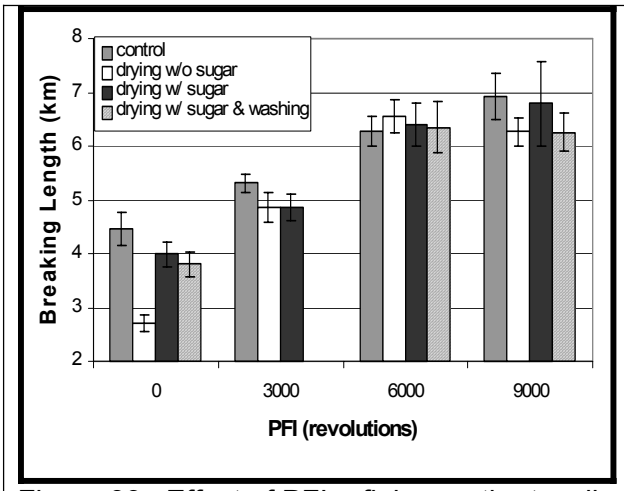

Figure 33. Effect of PFI refining on the tensile strength of recycled paper

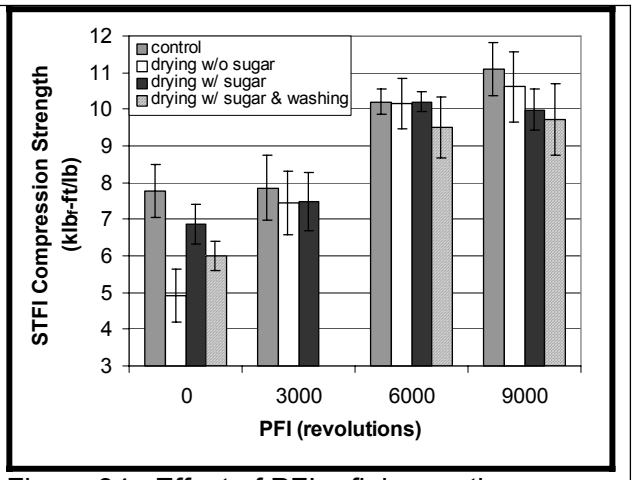

Figure 34. Effect of PFI refining on the compression strength of recycled paper

It is worth paying some attention to paper strength at the refining level of 6000 revolutions, since there is data for the fiber flexibility at that condition was shown in Fig. 31. Treated fibers still showed higher flexibility compared to untreated fibers, even under the condition of PFI refining, which was not consistent with the results of paper properties shown in

our previous work. In our previous work, we concluded that paper made from higher flexible fibers had greater strength compared to paper made from fibers having lower relative flexibility. One should recall that our previous work did not involve post-refining. Even in this study, if one only looks at the data without involving PFI refining, the results are completely consistent with previous work. One possible reason is that the fiber flexibility was not a dominant factor if there was additional refining. External fibrillation enhances sheets consolidation by entanglements of fibers during papermaking and enhances inter-fiber bonding. The process of refining increases external fibrillation. Compared to external fibrillation, the fiber flexibility contribution to the bonding between fibers may less significant, based on the present results.

CHRONOLOGICAL SUMMARY OF PROJECT ACTIVITIES

First quarter 2000: The award date for this project was February 28, 2000, and the end-date for the first reporting period was March 31, 2000.

In anticipation of the DOE project award, other discretionary funds at the University (McIntyre-Stennis) were used to assign a graduate student to do preliminary research work related to the project goals. Approximately $10,000 of discretionary funds were expended for the tuition, stipend, and insurance of Min Zhang between June 1999 and the end of February 2000 (when DOE funding was finalized).

Meetings were held with both industrial cosponsors. The first meeting, held at NC State University on October 8, 1999, included both Hercules, Inc. and International Paper. An additional meeting was held at International Paper on Feb. 17, 2000. At third project meeting was held with Hercules on May 16, 2000.

Results from the preliminary work were reported at the International Symposium on environmentally Friendly and Emerging Technologies for a Sustainable Pulp and Paper Industry, April 25-27, Taipei, Taiwan.

Candidate chemicals already screened by the end of the first reporting period included polyacrylate, guar solutions, glucose, sucrose, and higher-mass sugars. Work initiated during the quarter was focused on the screening of carboxymethyl cellulose samples of various charge density and molecular mass.

The experimental procedure for the screening tests involved the preparation of a uniform pulp batch by appropriate screening and refining. The refined pulp was characterized by formation into paper handsheets, using TAPPI standard procedures with certain modifications to better simulate the process of making linerboard for corrugated containers. The paper was dried on the standard polished rings, but these were placed in an oven at 105 ^{o}C for ten minutes to dry the paper to about 7% moisture before the sheets were equilibrated at the standard 50% humidity conditions. A basis weight of 120 g/m^2 was used instead of the standard 60 g/m^2 called for in the TAPPI methods for testing of paper. The handsheets were evaluated by standard physical test procedures. The STFI compression test is carried out as the primary criterion of strength potential of the handsheets. Additional tests included tensile breaking length, other tensile properties, and tear strength.

After evaluation of the physical properties, the fiber material was redispersed by means of a TAPPI disintegrator. A second cycle of papermaking was carried out in the same manner as the initial sheetmaking, without addition of further chemicals.

Figures 35 and 36 were published in the *Proceedings of the TAPPI Papermakers Conf.*, 2001. The figure at left illustrates the main procedure used in the screening tests that involved polymeric strength additives.

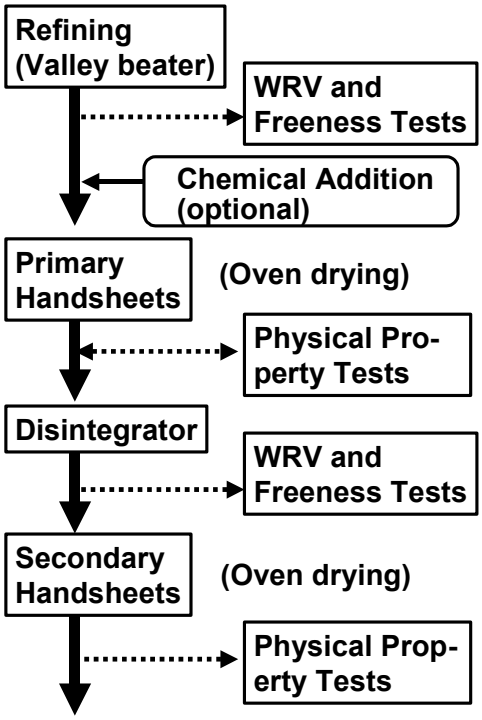

Figure 35. Procedure for evaluating the effects of various chemical additives

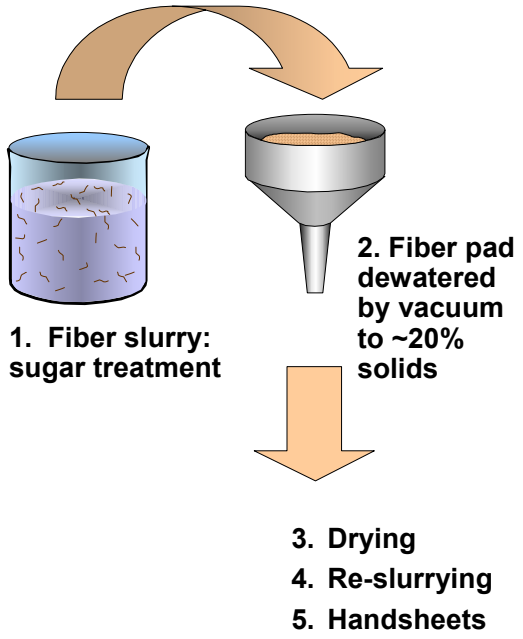

Figure 36. Special procedure for evaluation of the effects of sugars and dextrans, which are assumed to have no specific interaction with the fiber

Figure 36 describes an alternative procedure that was used for experiments dealing with the effects of potential "blocking" agents, *i.e.* sugar monomers and oligomers. These evaluations required that the "agent" be kept in a relatively high concentration during fiber treatment and dewatering. A procedure involving a Büchner funnel was used in place of the usual handsheet procedure for such determinations.

Second quarter 2000: The quarter's research activities were focused on screening experimentation with a variety of different candidate chemical pretreatments of refined, never-dried unbleached kraft fibers.

Results from some of the initial screening work are shown in Fig. 37. The vertical limits of each plotted bar show 95% confidence intervals of the data.

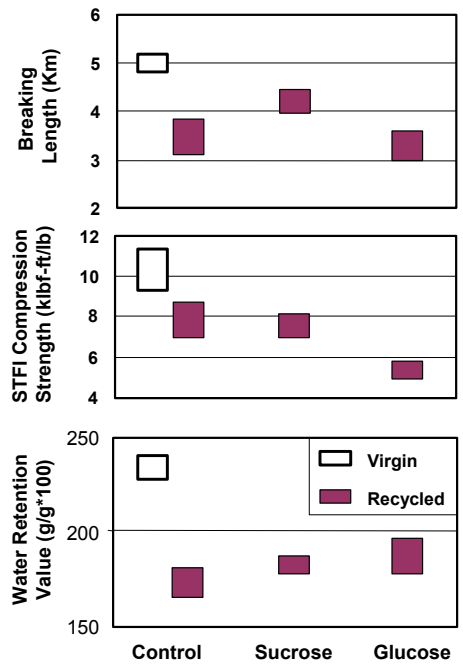

Fig. 37. 95% confidence limits for effects related to the presence of sugar solution during drying (special procedure to avoid rinsing)

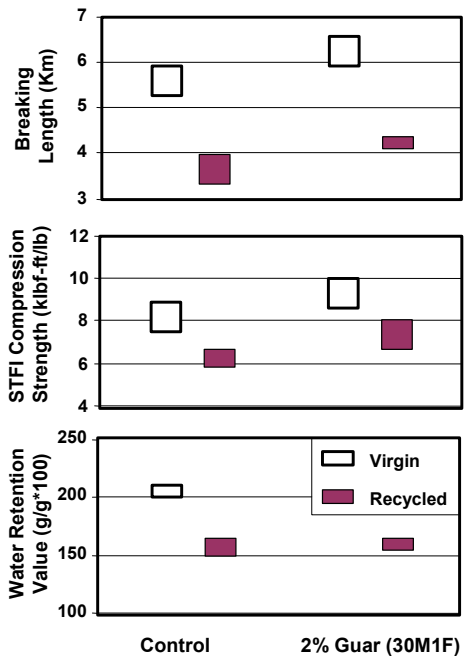

Fig. 38. 95% confidence limits for effects related to guar treatment before drying (usual handsheet method)

Figure 38 illustrates results for a polymeric additive, in this case one of the guar gum candidate materials.

Effects of the following chemicals were evaluated, either alone, or in selected combinations and orders of addition:

- Hemicellulose
- Five kinds of carboxymethylcellulose CMC (CMC7L, CMC7M, CMC7H, CMC9M8, CMC12M8)
- Poly-diallyldimethylammonium chloride DADMAC (low, high molecular weight)
- Orange dye
- Three kinds of fluorescent whitening agents(Di-, Tetra-, Hexa-sulfonated).

The most striking improvements in strength were achieved with combinations of the cationic polymer (poly-DADMAC) and one of the carboxymethylcellulose products. These treatments increased both the initial strength (first drying) and the strength of recycled sheets to which no further chemicals were added (second drying). The most promising results in terms of the recycled samples were achieved with sequential addition of the two chemicals to the pulp (not pre-mixing). Although the cationic polymer alone yielded a slight increase in the strength of the primary sheets, it hurt the strength when the same furnish was recycled. An anionic direct

dye and various fluorescent whitening agents all yielded significant increases in the strength of the recycled sheets. None of the CMC samples, when added alone, yielded any significant change in paper properties. Also, the hemicellulose, when added alone to the never-dried, refined pulp, had no significant effect on the paper.

The following major purchases (not including shipping charges) were made in order to support the project work: Centrifuge (for more accurate determination of water retention values) $3705 (our purchase order 473292 with university discount); rotor for centrifuge $759.60 (P.O. 473297); shaft adapter to attach the rotor to the centrifuge $162.24 (P.O. 00514447); and two analytical balances purchased out of the savings from the discounts from Fisher ($248,58 and $1196, respectively, included in P.O. 473297). As noted in the previous quarterly report, water retention value tests are used to compare the never-dried, refined pulp to the recycled pulp. This test gives an indication of the degree to which the recycled fibers may have lost some of their ability to swell and hold water. The loss of water retention value has been found to correlate with the ability of fibers to bond to each other.

Travel charges were expended for attendance at the project meeting with the cosponsors in Wilmington, DE on May 31, 2000. We were fortunate to be able to rent a state-subsidized aircraft to carry the whole group to our destination for about $700 (see accounting statements for accurate cost, including a van rental in Wilmington).

Third quarter 2000: This quarter's research activities were focused on screening experimentation with a variety of different candidate chemical pretreatments of refined, never-dried unbleached kraft fibers. Effects of the following chemicals were evaluated this quarter, either alone, or in selected combinations and orders of addition:

- Four types of starch: cationic, anionic, hydroxyethylated, and oxidized
- Three types of guar gum, some cationic, some used in combination with poly-DADMAC
- Sodium lauryl sulfate
- Chitosan of two molecular masses, alone and with carboxymethylcellulose (CMC)
- A CMC sample of lower charge density than prior samples screened

The most striking improvements in strength of recycled sheets were achieved with cationic starch and with a combination of poly-diallyldimethylammonium chloride (DADMAC) and CMC. Selected results from this work are shown in the figures that follow:

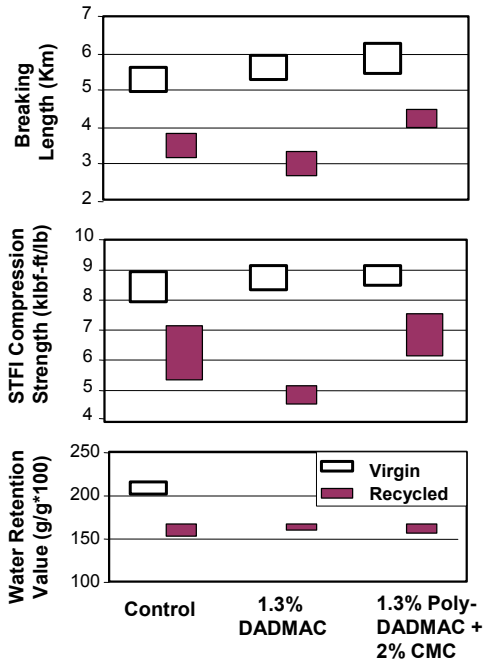

Figure 39. Demonstration of dual-treatment effect with positive, followed by negative polymer

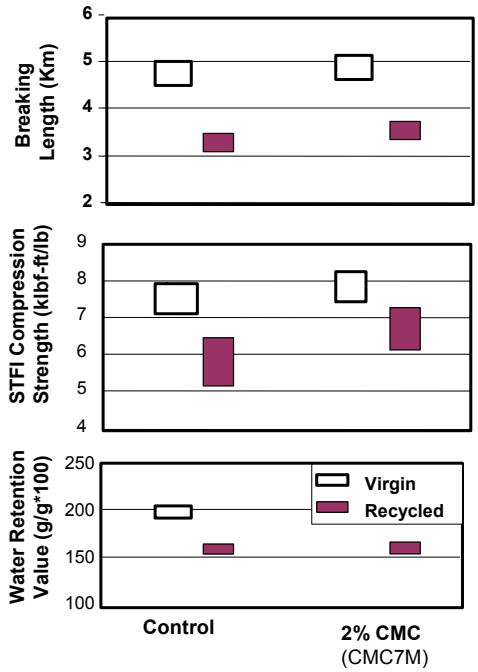

Figure 40. Demonstration that there was only a minor benefit (if at all) with negative polymer alone

Fourth quarter 2000: This quarter's research continued the screening experimentation with a variety of different candidate chemical pretreatments of refined, never-dried unbleached kraft fibers. In addition to these tests, work was done to clarify the mechanism of strength loss and its prevention or compensation. It was determined that sucrose was present at the 0.34% level by mass in sheets that had been formed from pulp dried in the presence of 10% sucrose. This amount of sugar remained in the recycled sheets in spite of the high dilution levels with fresh water when making handsheets.

Data were evaluated to determine characteristic effects of different classes of chemical additives, and also as a means of selecting leading candidates that will provide the main focus for work in 2001. Results of analysis of data from over 60 different treatment conditions, each with replicate tests and controls, showed that the most promising candidates were all polymeric agents or combinations with molecular weights in the hundreds of thousands. STFI compression was used as the lead determinant of linerboard performance. The STFI compression strength of recycled pulp was benefited most in the case of pre-treatment of the never-dried pulp with cationic water-loving polyelectrolytes such as chitosan, cationic starch, and cationic guar, either alone or in a sequential addition with an oppositely charged polyelectrolyte such as carboxymethylcellulose (CMC). The list was quite different if breaking length was used as the criterion; the highest breaking length values for the recycled sheets were achieved with a combination of polyDADMAC and CMC, or with an anionic direct dye at

high concentration, or with a hydroxyethylated starch pretreatment of the pulp before it was dried the first time.

First quarter 2001: Much of the work completed during the quarter was described in the *Appita J.* article (Vol. *55,* no. 2, 2002). In brief, our research identified two strategies to overcome the loss of compression strength that results from drying and reslurrying unbleached kraft fibers.

- The first strategy involves incorporation of certain low-molecular-mass species within the cell walls of fibers. Results of our experiments imply that both the size of the molecule and details of its chemical nature are important. Our results also are consistent with an ability of sucrose and similar materials to inhibit closure of submicroscopic pores in the walls of kraft fibers when they are dried, helping the fibers to retain a great fraction of their original bonding potential. It is of practical importance to know the reason for the loss of bonding potential of kraft fibers, when they are dried, since this information can suggest how different papermaking process factors are likely to affect the strength of recycled papers.
- The second strategy involves addition of polyelectrolytes with sufficiently high molecular mass and other suitable properties that they remain at the outer surfaces of fibers, even when they are recycled. Strength benefits were observed both in the virgin handsheets, and particularly when recycled handsheets were compared to "control" recycled handsheets that had not been treated before the first drying. Cationic starch yielded especially interesting results, since the relative benefits were even more promising in the recycled paper, compared to the relative benefits in the virgin paper (each time comparing the results to control sheets with the same drying history). Also, there seemed to be a lot of promise in cases where the never-dried pulp had been treated sequentially with oppositely charged polyelectrolytes.

Figures 41-42 show some of the results that were reported in the peer-reviewed article (published in *Appita J. 55,* issue 2, 2002):

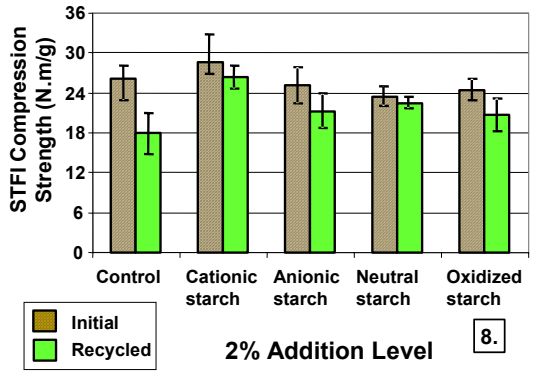

Figure 41. Compression strength of virgin and recycled fibers as affected by the addition of various candidate chemicals at the 2% level.

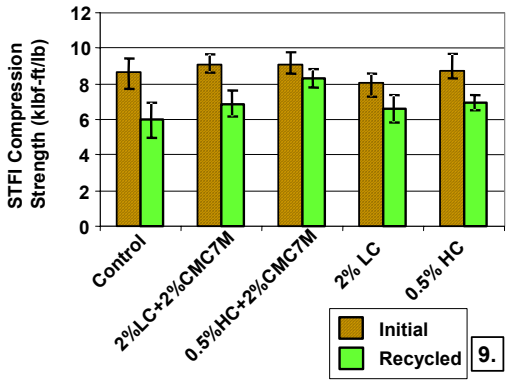

Figure 42. Compression strength of virgin and recycled fibers as affected by chemicals treatments including chitosan

Second quarter 2001: Work during the second quarter 2001 focused on quantifying and understanding how temperature and drying affect kraft fibers. Based on previous work in our group and by others, we already knew that drying of kraft fibers tends to reduce (a) the tendency of the fibers to hold water (WRV), and (b) the ability of the fibers to bond together. However, it was not known to what extent the drying of paper might also affect the degree of polymerization of the cellulose molecules themselves. Our results this quarter demonstrated the following:

- Heating of kraft fibers in the absence of drying can have a very significant effect on the molecular mass of the cellulose. For example, heating under pressure at 150 degrees Celsius for 15 minutes caused the relative molecular mass of cellulose (determined by cupriethylenediamine solution viscosity) to decrease from 17 to 11 centipoise viscosity units.
- By contrast, ordinary drying of another set of handsheets at 105 degrees Celsius had no significant effect on the viscosity numbers.
- Water retention values were decreased to a greater extent when the fibers were allowed to dry, compared to when they were kept wet during the heating.

Our working hypothesis, to explain these results, was that the observed molecular breakdown of the cellulose must be mainly a chemical effect. If loss of cellulose molecular mass had been due to a mechanical effect, then one would anticipate relatively large effects due to the stresses induced by drying. In fact, almost the opposite trend was observed: little if any cellulose degradation occurred in the case of dried handsheets, even if they were exposed to 175 degrees Centigrade for 15 minutes. Further evidence in favor of a chemical effect was the fact that increasing temperature yielded an increasing effect on cellulose molecular mass in the absence of drying.

A second working hypothesis was that the observed changes in water retention value are mainly controlled by mechanical factors, at least under the conditions of these recent tests. A mechanism dominated by capillary forces, tending to irreversibly close submicroscopic pores in the cell walls of kraft fibers when they are dried, would be consistent with the following observation: The recent data suggest that drying itself, regardless of temperature, has the major effect on water retention values, and that the temperature during drying has a relatively small additional contribution to the fiber's loss of water-holding ability.

Issues of temperature during drying are important for papermakers in light of the common practice of over-drying. For instance, it is common to dry paper well below its shipping moisture in order to be able to correct for moisture streaks. In such cases the paper is partly rewetted by spray application or with a water-box at the calender stack. Another reason that papermakers over-dry paper is to cure certain sizing agents or wet-strength resins. The new results obtained this quarter don't give a complete picture, but they do raise a concern that the hot, wet conditions in a paper machine dryer section might be degrading the molecular mass. On the other hand, they help to reduce any concern that over-drying is having a major effect on the changes in fiber porosity that we usually associate with a reduced flexibility of the cellulose fibers.

Other activities this quarter included the following:

- Min Zhang, the Ph.D. candidate assigned to the work, prepared a preliminary research proposition, including a literature review, a proposed hypothesis, and a set of research aims

designed to clarify the mechanism of bonding strength loss and the ways it can be minimized. One of the things that has come out of this process is a realization that water retention values (WRV), may not be giving us sufficiently detailed information about what is happening the micro-pores in the cell walls of kraft fibers during drying. Equipment was assembled for follow-up work with inverse size-exclusion chromatography (ISEC), a method that can provide information about the pore size distributions, not just the total amount of water contained in those pores.

- Erik Welf, an undergraduate student in NC State University's Wood and Paper Science program carried out the initial work involving cellulose molecular mass and the effects of wet-heating versus drying at various temperatures. Raymonda Barbour, an undergraduate from the University of Virginia, continued the work, starting at the end of May. This work was continued through most of July.

Third quarter 2001: Work during the third quarter 2001 was devoted mostly to issues raised by our corporate partners. Some further tasks were in response to input during a meeting with the AF&PA committee. It was proposed by several people that we might be overlooking some unknown opportunities of papermakers to avoid strength losses by some relatively simple adjustments of factors such as drying temperatures or pH values. Studies involving the temperature and time of heating and drying already were started during the second quarter. New work started during the third quarter extended the scope of the project to include adjustments in the pH and wet-pressing conditions.

A main conclusion of the work during the third quarter 2001 was that pH before the initial papermaking operation did *not* have a major effect on the compression strength of either the virgin sheets or the recycled sheets. Neither did pH have a significant effect on water retention values over the range that we studies. This new information would not have been predicted from the previous literature. In fact, a previous report by Lindstrom and Carlsson suggests that increasing pH ought to yield more highly swollen pulp (*Svensk Papperstidn. 85,* 15: 146, 1982), and one might assume from this that it would yield higher bonding ability. However, the differences between the two sets of results appeared to be consistent with different conditions used to prepare the pulps. The cited study involved pulps that had been subjected to a series of buffering treatments at low and high pH to remove all of the divalent or trivalent metal ions. Such a treatment is expected to make the pulp less representative of what happens in a typical paper machine system. By contrast, our work was carried out with rinsed pulp with no replacement of ions.

Tests were carried out to determine the effect of drying temperature on the swelling ability of kraft fibers, as well as the degree of polymerization of the cellulose molecules in those fibers. Swelling is of concern to us because, based on past work, one expects more highly swollen fibers to be more flexible and to be more able to conform to each others' surfaces in the formation of inter-fiber bonds. The degree of polymerization is of concern to us only if it is enough to weaken the individual fibers so that they break more frequently during paper strength tests. Very little information was available regarding effects of heating and drying on cellulose molecular mass. In an effort to obtain the most accurate information about cellulose molecular weight, much of this work was carried out with bleached kraft pulp.

With respect to fiber swelling, we measured the effects of heating and drying on water-retention values (WRVs). In the case of bleach kraft we observed a relatively large drop in

WRV results due to drying, regardless of the temperature. For example, drying at room temperature in a 50% relative humidity environment (TAPPI standard conditions) yielded a reduction in WRV from 176 to 129 percent water in fiber. Heating at various temperatures up to 120 °C yielded only a modest further reduction in WRV to 122%. "Over-heating" to 175 °C yielded a WRV of 105%. Similar results were obtained in the case of unbleached kraft pulp – an initial large drop in WRV due to drying at room temperature. An increase in drying temperature over the range 25 to 120 °C had little further effect on WRV. Further heating to 175 °C yielded a decrease in WRV of the dried pulp from about 125% to 108%. The general conclusion that we could draw from this work was that some pore closure can be expected with southern US unbleached kraft pulp even when the drying conditions are very mild. Further decreases in swelling ability are expected to be moderate, and mainly limited to extreme cases of over-drying or hot storage. Figure 43 shows an example of this type of result.

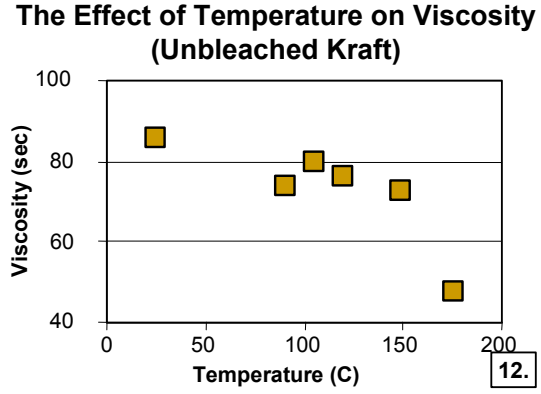

Figure 43. Effect of drying temperature on viscosity of unbleached kraft pulp

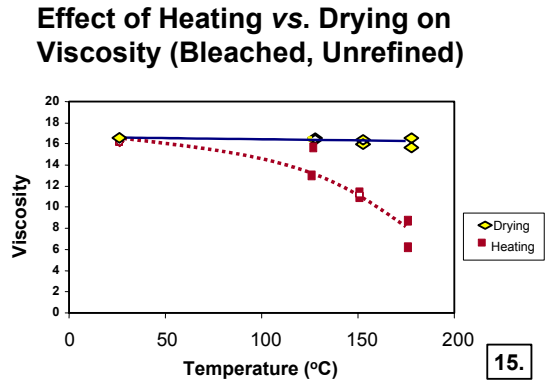

Figure 44. Effect of heating only, *vs.* drying on the viscosity of bleached kraft pulp

With respect to loss of molecular mass, the results of the cellulose viscosity determinations showed effects only at times and temperatures exceeding those present during the conventional drying of paper. In the case of bleached kraft the most dramatic losses in molecular mass were obtained only when the pulp was incubated under pressure, to avoid drying. When drying was allowed, no significant loss of degree of cellulose viscosity was observed in the range from room temperature to 150 °C. Further heating to 175 °C (in the case where drying was allowed) caused a discernable drop, but it still could not be demonstrated with high statistical confidence. Similar results were obtained with unbleached kraft pulp, except that there was a significant loss in viscosity when comparing pulp dried at 175 °C versus 150 °C or lower. The general conclusion from this work was that only in the case of extreme over-drying or hot storage is a loss of molecular mass likely to be an issue. The conditions that have been used in our laboratory work so far are well below the temperature that caused a loss of molecular mass. Various estimates have been made of the ultimate temperature of paperboard during drying; however, it appears unlikely that commercially produced linerboard would experience temperatures above 150 °C.

The summary report from the previous quarter stated our hypothesis that the loss of molecular mass upon heating (without drying) was mainly a chemical effect. In particular it was hypothesized that cellulose chains were cleaved by hydrolysis, a reaction that one would expect to become more important with decreased pH. A question that we sought to answer during the third quarter 2001 was whether significant loss of cellulose molecular mass is likely to occur during conventional drying of linerboard over a range of pH conditions. The pH conditions evaluated are listed in the following table, together with reasons underlying the selection of those pH values:

pH Value	Reasons for Selection
3.0	Low enough to protonized most of the COOH groups
4.5	Intermediate “acidic papermaking” condition
6.0	A common pH value for linerboard production
8.0	A full “alkaline papermaking” condition

The effect of pH during drying on cellulose viscosity first was evaluated in the case of bleached pulp. Resulting viscosities were lower after drying at the two lower pH values (3.0 and 4.5), compared to the two higher values (6.0 and 8.0). Regardless of pH, samples dried at 105 ^{o}C suffered greater losses in viscosity than samples dried under TAPPI standard conditions. For instance, the viscosity of cellulose from pH=4.5 sample that was dried in the oven fell from an initial value of about 19 to a final value of about 17.

In the case of the unbleached kraft pulp no significant effect of pH during drying was observed, relative to cellulose molecular mass. However, it is worth noting here that a special procedure was required in order to estimate the cellulose molecular mass in the unbleached kraft pulp. The first step involved removal of lignin with sodium chlorite, acetic acid, and 24-hour soaking. It is not known whether this additional step might have obscured small differences between the samples as a result of drying at different pH values.

Another activity during the third quarter was the setting up of an apparatus for analysis of pore size distributions by inverse size-exclusion chromatography (ISEC). Our interest in using this method is prompted by uncertainties about the water retention value (WRV) test results. One problem with the WRV data is that they estimate only the total amount of water held by the fibers; they don’t say anything about where this water is located. It is not even clear whether all of the water detected by the WRV test is within the fiber walls; it is reasonable to expect that some of it may be associated with surface fibrillation and with gelatinous polymers adsorbed at the fiber surface. By contrast, the ISEC test is capable of showing the distribution of pore sizes (by total pore volume) within a pulp sample.

Fourth quarter 2001: Work during the fourth quarter 2001 was mainly in two areas: (1) a more comprehensive evaluation of how fibers change as a result of drying, either at room temperature or at elevated temperature; and (2) continuing preparation of laboratory equipment for analysis of fiber porosity and effects of conditions prior to drying on fiber porosity when the pulp is redispersed in water.

Results shown in Table 5 were from the first of these activities:

Table 5. Effects of Drying in the Absence of Chemical Treatment (Baseline)

Handsheet dried condition		**Air-Oven**		**Oven-Oven**	
Test	Unit	Refined only	*Recycled*	Refined only	*Recycled*
Freeness	ml	426	------	426	-------
Basis Weight	g/m^2	124.0	*122.2*	126.3	*126.4*
Thickness	10^{-3} in	6.3	*7.0*	6.5	*7.3*
Density	g/cm^3	0.77	*0.69*	0.76	*0.68*
Tear Strength	g_f	175.3 ± 24.0	*215.3 ± 11.8*	182.7 ±19.7	*226.3 ± 22.9*
Breaking Length	Km	6.151±0.422	*5.472±0.361*	7.023±0.472	*5.379±0.271*
STFI Compression	klb_f-ft/lb	10.77±0.844	*8.460±0.624*	9.981±0.901	*8.428±0.568*
WRV	%	244.2 ± 6.3	*186.5 ± 5.4*	238.1 ±13.7	*181.5 ± 7.7*
Light Scatt. Coeff.	m^2/Kg	9.10 ± 1.21	*10.42 ± 0.96*	7.74 ± 0.97	*10.47 ± 1.21*
Zero-Span Tensile	Km	34.8 ±1.2	*36.4 ± 3.2*	35.1 ± 3.0	*39.3 ± 1.9*
Fiber Length*	mm	1.81 ± 0.07	*1.76 ± 0.06*	1.77 ± 0.07	*1.75 ± 0.06*
Fiber Length**	mm	1.29	*1.21*	1.30	*1.21*
Fines (# average)	%	30.48	*33.49*	28.40	*32.67*
Curl		0.064±0.004	*0.053±0.003*	0.060±0.004	*0.053±0.003*
Moisture	%	9.5	-----	10.0	-----
Conductivity	μs	367	*367*	366	*363*

Notes:
*: In this row "fiber" is defined as having length greater than 0.2 mm; by that criterion the average never-refined fiber length was 2.15 mm.
**: In this row "fiber" is defined as having length greater than 0.07 mm; by that criterion the never- refined fiber length averaged 1.68 mm.

First quarter 2002: Work during the first quarter 2002 was mainly related to fiber flexibility testing. Also there were continued efforts to prepare laboratory equipment for analysis of fiber porosity and effects of conditions prior to drying on fiber porosity when the pulp is redispersed in water. Table 6 shows an example of fiber flexibility results:

Table 6 Drying Effect on Fiber Flexibility			
Sample	**Average**	**Median**	**3rd Quartile**
UDUR pulp	5.38E+11	3.51E+11	6.64E+11
ADUR pulp	4.43E+11	2.12E+11	4.90E+11
ODUR pulp	1.48E+11	3.70E+10	9.70E+10
UD: Never Dried; **AD**: Air Dried; **OD**: Oven Dried; **UR**: Unrefined			

Tests were initiated to look at the effect of pH. This work was still in progress at the end of the reporting period, so there was not yet any data corresponding to dried fibers. However, pH already was found to have a strong effect on fiber flexibility before the fibers were dried. Flexibility increased with increasing pH. This is shown in Table 7:

Table 7. Effect of pH on Fiber Flexibility

Sample	Average	Median	3rd Quartile
UDUR @pH3	5.91E+11	3.32E+11	8.61E+11
UDUR @pH4.5	8.21E+11	4.98E+11	8.35E+11
UDUR @pH6	11.5E+11	6.82E+11	13.0E+11
UDUR @pH8	11.1E+11	6.84E+11	13.1E+11
Note: **UD**: Never Dried; **UR**: Unrefined			

Recent work also revealed a pronounced twisting of fibers that had been exposed to oven-drying conditions. This is shown in Figs. 45 and 46, which compare a wet never-dried fiber and a wet oven-dried fiber that had been subsequently handled according to the procedures for evaluation of fiber flexibility:

Figure 45. Light-micrograph of unbleached kraft fiber after drying at 105 °C.

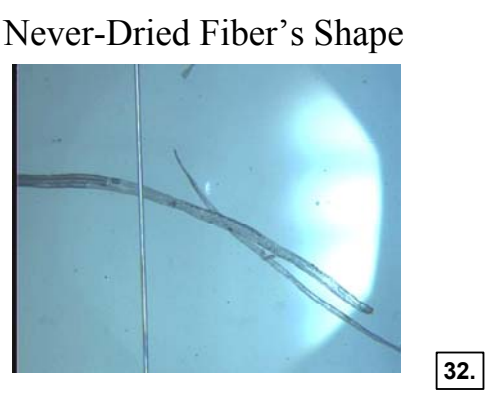

Figure 46. Light-micrograph of (previously) never-dried fiber during flexibility analysis

In each case the vertical, straight object is a stainless steel wire used for the flexibility analysis. The flexibility results and twisting results have important potential implications regarding paper strength and density. Future work is planned to follow up on these observations.

PRODUCTS OF PROJECT AND TECHNOLOGY TRANSFER

Research sponsored by this project (DE-FC07-00ID13878) contributed toward eight publications, as shown below. In the following list the asterisk ahead of the first author name indicates each peer-review journal article.

A. Publications (with abstracts)

* Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., “Effect of Refining on Changes to Sugar-Treated Kraft Fibers during Recycling,” in preparation.

> The addition of sugar to refined, never-dried softwood kraft fibers before drying showed that the sugar treatment improved the strength of recycled paper made from the corresponding re-slurried fibers. Results from fiber flexibility tests showed that the sugar-treated fibers were more flexible, compared to untreated fiber. Tests of fiber length and fines content by image analysis (Fiber Quality Analyzer) also showed that untreated fibers tended to generate more fines and become shorter during dispersing in a TAPPI disintegrator after air-drying. Since, based on the previous literature, one should not expect a significant effect for a disintegrator to either reduce fiber length or create new fines during dispersing, we then examined the effect of severe drying (oven drying at 105 °C for 30 minutes) on fiber length and fines content during dispersing. However, if fiber pads that made from sugar-treated fibers were oven dried, and then refined before making recycled paper, no significant differences of paper strength were found in the recycled papers compared to the control experiment, and fiber length either, as well as fines content. Results from the fiber flexibility test showed that treated fibers still have higher flexibility compared to untreated fibers. The results indicated that mechanical force (refining) might have a dominant effect on fiber fibrillation and fines generation, and that the effects of refining can be obscure the influence of drying on the bonding properties and morphology of the fibers.

* Hubbe, M. A., Venditti, R. A., Barbour, R. L., and Zhang, M., "Changes to Unbleached Kraft Fibers Due to Drying and Recycling," *Progress in Paper Recycling 12* (5): 00 (2003), in print.

> Drying of unbleached kraft pulp in the laboratory revealed two main stages in its response to increasing temperature of drying. The first stage was characterized by significant decreases in water retention value, capacity to adsorb a cationic polymer, dry strength, and apparent density of handsheets formed after re-slurrying the pulp with no additional treatment. These changes, which were independent of the drying temperature, were attributed to the action of capillary forces in the closure of micro-pores in the cell wall during the initial drying. The second stage was characterized by further significant decreases in all of the same parameters when drying temperatures became as high as 150 to 175 oC. In addition, high-temperature drying also resulted in a loss of molecular mass of the cellulose, as revealed by viscosity tests. Surprisingly, neither cellulose molecular mass nor water retention was affected to a significant extent by the value of pH prior to drying, within a range of 3 to 8. The results suggest that whereas some

irreversible changes in fiber properties are unavoidable during conventional papermaking practices, further losses in the bonding ability of unbleached kraft fibers can be caused by over-drying.

* Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "The Prevention of Strength Loss of Recycled Paper by the Addition of Sugar during the Initial Drying or Virgin Unbleached Kraft Pulp Fibers," *J. Pulp Paper Sci.*, submitted.

It is known that paper made from recycled, chemically pulped fibers typically has a lower strength compared to paper made from virgin fibers. In the case of unbleached softwood kraft pulp it was confirmed in this study that the paper strength (tensile strength and compression strength) decreased after recycling. The addition of low molecular weight chemicals to virgin pulp before ever drying was evaluated to determine the potential for preventing paper strength loss upon recycling. The results showed that sugars such as sucrose and glucose at high concentration could improve the recycled paper strength compared to a control experiment with no sugar added. Limited published information is available showing how the flexibility of recycled fibers, in the re-wetted state, is related to the chemical conditions before they were first dried. Fibers treated by sugars were found to have a higher flexibility than untreated fibers, as well as higher water retention values.

* Welf, E., Venditti, R. A., and Hubbe, M. A., "The Effect of Heating and Drying on the Properties of Recycled Papermaking Fibers," in preparation

The effects of heating and drying bleached kraft fibers were separately investigated by measuring the water retention value (WRV) and cellulose viscosity. Heating and drying were observed to result in different changes in fibers upon treatment. Heating fibers without water removal resulted in a decrease in WRV from the never-dried and air-dried levels, but not as large of a decrease as drying at high temperatures. Drying at high temperatures reduced the cellulose viscosity only slightly, whereas heat treatment without allowing water loss resulted in much greater losses in cellulose viscosity. Refining was observed to have little effect on the measured changes in fibers.

* Hubbe, M. A., Jackson, T. L., and Zhang, M., "Fiber Surface Saturation as a Strategy to Optimize Dual-Polymer Dry Strength Treatment," *TAPPI J*,. submitted.

The compression strength of unbleached kraft handsheets was maximized when the first component of a dual-polymer treatment was added at a level corresponding to saturation of the fiber surface. The saturation level of poly-diallyldimethylammonium chloride (poly-DADMAC), determined by streaming current analysis, also coincided with a maximum in water retention value (WRV) and a minimum in the light scattering coefficient of the paper. Idealized descriptions of the polymer interactions are proposed to help explain the observations. The principles and methods used in the present study have potential to be used for optimizing or controlling dual-polymer treatments in cases where the goal is to maximize the strengthening effect.

* Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Can Recycled Kraft Fibers Benefit from Chemical Addition Before They Are First Dried?," *APPITA J. 55* (3): 135 (2002)

> Over 50 chemical treatments of never-dried pulp were compared relative to the strength of paper made subsequently after the fibers had been dried and recycled once. Treatments having the greatest beneficial effect on the compression strength of recycled unbleached kraft paper tended to be polyelectrolytes of relatively high molecular mass. Many of the most effective treatments, either alone or by sequential addition, included both cationic and anionic functional groups on the polymers. Results were consistent with the persistent nature of charged complexes formed by polyelectrolytes at fiber surfaces, and the contribution of such complexes to inter-fiber bonding, even after drying and recycling.

Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Effect of Chemical Pretreatments of Never-Dried Pulp on the Strength of Recycled Linerboard," *Proc. TAPPI Papermakers Conf*., 2001.

> According to the American Forest and Paper Association (AF&PA) the recovery rate of corrugated boxes used in the US now exceeds 75%. In principle the recycling of boxes saves fiber resources and requires less total energy. However, further progress in old corrugated container (OCC) recycling faces a potential barrier. It is known that recycled kraft fibers have a reduced bonding ability. The approach taken in this study was to pre-treat the never-dried fibers before the first cycle of papermaking. New data have been obtained with never-dried, refined, unbleached kraft pulp. Simple drying, low-shear disintegration, and forming without further refining yielded a loss in compression strength in the range 19 to 26%, depending on the pulp batch. Pretreatment with various chemical agents was able to compensate for some of the strength loss. Two general classes of treatment agent were identified that were able to favorably affect the strength of recycled sheets. Certain low-molecular weight materials such as sucrose appeared to interfere with the mechanism of pore closure during the initial drying. In contrast, certain high-mass polyelectrolytes such as guar gum products, cationic starch, and polyelectrolyte complexes appeared to affect the adhesiveness of the fiber exteriors of the repulped fibers.

Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Loss of bonding Strength Dye to Drying and Repulping of Kraft Fibers: Effects of Chemical Additives," *Proc. International Symposium on Environmentally Friendly and Emerging Technologies for a Sustainable Pulp and Paper Industry*, Taipei, Taiwan, April 25-27, 2000.

> Chemical pretreatment of never-dried kraft fibers was found to improve the strength of recycled paperboard. Lab tests with guar gum added to unbleached softwood kraft pulp (linerboard furnish) showed that the additive increased the tensile strength and resistance to compression failure. Strength values fell by 25-35% when the same fibers were reslurried and then formed into second generations of paper. However, the strength of the paper made from pre-treated fibers remained significantly higher than the

recycled, untreated control. The results suggest a strategy whereby an initial additive or additives to never-dried fibers yield strength benefits that persist over at least one generation of recycled paper. Expected benefits include reduced overall costs for strength-enhancing chemicals, reduced basis weight requirements to achieve product strength requirements, and an ability to use higher levels of waste fibers.

Tests were carried out to shed light on the mechanism of strength loss and the effects of chemicals relative to strength loss when paper is dried and then recycled. The chemical effects on strength appeared to be governed by at least two significant mechanisms. For instance, it was found that pretreatment of the never-dried pulp with a very high level of sucrose yielded an improvement of the tensile strength of recycled paper, compared to untreated fibers that were dried and recycled. This observation is consistent with the known ability of sucrose to penetrate into the fine pores in the walls of kraft fibers. The sucrose-pretreated fibers retained higher levels of water retention value (WRV), indicating a greater degree of swelling when the once-dried fibers were placed back into water. These results with sucrose are consistent with a mechanism in which loss of bonding ability is related to irreversible closure of pores in the fiber cell wall. Contrasting results were obtained when the never-dried fibers were treated with underivatized guar gums. The guar increased the relative strength of both the primary and secondary sheets, but there was no effect on the water-holding ability of the fibers. It is proposed that the guar's mechanistic role is related to its effects on relative bonded area or shear strength of bonds per unit of bonded area.

B. Website

While the publications listed above are the primary means of communicating project results, the results are also publicized (including abstracts of already-published articles) in the following website: http://www4.ncsu.edu/~hubbe/index.htm

C. Other

The following conference papers also included presentations in front of technical and scientific audiences:

- Welf, E., Venditti, R. A., and Hubbe, M. A., “The Effect of Heating and Drying on the Properties of Recycled Papermaking Fibers,” presented by Eric Welf, April 6, 2001 as part of an undergraduate research symposium.
- Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Effect of Chemical Pretreatments of Never-Dried Pulp on the Strength of Recycled Linerboard," *Proc. TAPPI Papermakers Conf.*, 2001, presented by Min Zhang.
- Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A., "Loss of bonding Strength Dye to Drying and Repulping of Kraft Fibers: Effects of Chemical Additives," *Proc. International Symposium on Environmentally Friendly and Emerging Technologies for a Sustainable Pulp and Paper Industry*, Taipei, Taiwan, April 25-27, 2000, presented by Martin Hubbe.

D. Patent applications, licensing agreements

No patents have been applied for.